

JPRS-UMS-88-002

11 JANUARY 1988



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# ***JPRS Report***

# **Science & Technology**

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***USSR: Materials Science***

11 JANUARY 1988

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SCIENCE & TECHNOLOGY  
USSR: MATERIALS SCIENCE

CONTENTS

ANALYSIS, TESTING

|                                                                                                                                                                                                                                                           |   |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| Kinetic Laws Governing High-Temperature Oxidation of Industrial Ti Alloys<br>(G. G. Maksimovich, V. N. Fedirko, et al.; KIZIKO-KHIMICHESKAYA MEKHANIKA MATERIALOV, No 6, Nov-Dec 86).....                                                                 | 1 |
| Fatigue Fracture of Runner Blades Made of Heat-Resistant Cast Ni-Cr Alloys in Gas-Turbine Engines<br>(I. A. Makovetskaya, O. I. Marusiy, et al.; PROBLEMY PROCHNOSTI, No 1, Jan 87).....                                                                  | 2 |
| Temperature and Orientation Dependence of Momentary Strength Characteristics, Young's Modulus, and Linear Expansivity of Single Crystals of ZhS6F Heat-Resistant Alloy<br>(I. L. Svetlov, N. N. Sukhanov, et al.; PROBLEMY PROCHNOSTI, No 1, Jan 87)..... | 3 |
| Changes in Mechanical Characteristics of Molybdenum Caused by Thermochemical Treatment<br>(L. P. Skuratov, V. K. Yatsimirskiy, et al.; PROBLEMY PROCHNOSTI, No 1, Jan 87).....                                                                            | 5 |

|                                                                                                                                                                                                                                                      |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Acoustical Characteristics of Invar Powder Alloys<br>(V. A. Vershinin, V. I. Kostikov, et al.; POROSHKOVAYA<br>METALLURGIYA, No 1, Jan 87).....                                                                                                      | 6  |
| Optical Characteristics of Y <sub>2</sub> O <sub>3</sub> -Eu <sub>2</sub> O <sub>3</sub> Films Produced by Ion<br>Bombardment of Hot-Pressed Targets<br>(A. F. Andreyeva, M. A. Katsitadze, et al.;<br>POROSHKOVAYA METALLURGIYA, No 1, Jan 87)..... | 7  |
| Defectoscopic Characteristics of Small Betatron MIB-4<br>(D. A. Boyko, A. A. Filimonov, et al.; DEFECTOSKOPIYA,<br>No 1, Jan 87).....                                                                                                                | 8  |
| Tungstenless Hard Alloy on TiC Base Produced by Various Methods<br>(V. K. Vitryanyuk, A. F. Kolchik, et al.; POROSHKOVAYA<br>METALLURGIYA, No 1, Jan 87).....                                                                                        | 9  |
| Induced Radioactivity of Steel Parts During Industrial<br>Defectoscopy With Electron Accelerators<br>(V. V. Varnavskiy, P. P. Zolnikov; DEFECTOSKOPIYA,<br>No 1, Jan 87).....                                                                        | 10 |
| Analysis of Smelting Processes for Reduction of Titanium-<br>Magnetite Ore Pellets<br>(Yu. A. Deryabin, Yu. S. Shchekalev; IZVESTIYA<br>VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA,<br>No 2, Feb 87).....                                   | 11 |

#### COATINGS

|                                                                                                                                                                                                                      |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Successive Boron-Chromium Impregnation of Carbon Steels<br>(V. D. Kalner, M. G. Karpman, et al.; FIZIKO-<br>KHIMICHESKAYA MEKhanika MATERIALOV, No 6, Nov-Dec 86)..                                                  | 12 |
| Combined Corrosive and Frictional Wear of Medium-Carbon Steel<br>With Eutectic Coatings in Salt Solution<br>(V. M. Golubets, G. A. Preys, et al.; FIZIKO-<br>KHIMICHESKAYA MEKhanika MATERIALOV, No 6, Nov-Dec 86).. | 13 |
| Plasma Metallization of Refractory Carbide Powders<br>(Ye. B. Koroleva, N. A. Klinskaya, et al.; FIZIKA I<br>KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86).....                                                    | 15 |
| Air Plasmatron PNV-23 for Deposition of Coatings<br>(M. V. Karasev, V. S. Klubnikin, et al.; AVTOMATICHESKAYA<br>SVARKA, No 1, Jan 87).....                                                                          | 16 |
| Deposition of Coatings of Self-Fluxing Alloy by Means of<br>Gas-Air Plasma<br>(D. A. Demchuk, S. Ya. Shekhter, et al.; AVTOMATICHESKAYA<br>SVARKA, No 1, Jan 87).....                                                | 17 |

|                                                                                                                                                                                                                          |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Increasing Productivity and Scope of Laser Hardfacing<br>(N. N. Odintsov, L. A. Shternin, et al.; SVAROCHNOYE<br>PROIZVODSTVO, No 2, Feb 87).....                                                                        | 18 |
| Structure and Properties of Anticorrosive Wear-Resistant<br>Coatings Produced by Plasma Hardfacing With Powder Materials<br>(E. S. Komarcheva, L. G. Mishchenko, et al.; SVAROCHNOYE<br>PROIZVODSTVO, No 2, Feb 87)..... | 19 |
| Plasma-Deposited TiC Coatings<br>(V. B. Raytses, V. M. Litvin, et al.; SVAROCHNOYE<br>PROIZVODSTVO, No 2, Feb 87).....                                                                                                   | 20 |

#### COMPOSITE MATERIALS

|                                                                                                                                                                                                      |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Nondestructive Method of Determining Critical Loads for Beams,<br>Plates, and Shells Made of Composite Materials<br>(V. P. Georgiyevskiy, I. S. Malyutin; PROBLEMY<br>PROCHNOSTI, No 1, Jan 87)..... | 21 |
| Resistance of Polymer Composite Materials to Interlaminar<br>Shear at High Temperatures<br>(A. V. Kudryavtsev; PROBLEMY PROCHNOSTI, No 1, Jan 87).                                                   | 22 |
| Modeling Compaction Process for Production of Fibrous Composite<br>Materials<br>(FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 1,<br>Jan-Feb 87).....                                                    | 23 |
| Composite Materials Based on Hydrogen-Absorbing Intermetallic<br>Compounds<br>(M. M. Antonova, T. I. Brataninch, et al.; POROSHKOVAYA<br>METALLURGIYA, No 2, Feb 87).....                            | 24 |

#### CORROSION

|                                                                                                                                                                                     |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Corrosion Resistance of Sintered Alloy Steels<br>(P. N. Ostriuk, I. I. Grigorichuk, et al.; IZVESTIYA<br>VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA,<br>No 2, Feb 87)..... | 26 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

#### FERROUS METALS

|                                                                                                                                                                                                                                 |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Desulfurization of Metal During Smelting of Extra-Low Carbon<br>Steel in Acid Converters<br>(D. Ya. Povolotskiy, O. K. Tokovoy, et al.; IZVESTIYA<br>VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA,<br>No 2, Feb 87)..... | 27 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|



## NONFERROUS METALS, ALLOYS, BRAZES, SOLDERS

|                                                                                                                                                                                                       |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Lengthening Service Life of Evaporators Made of Tungsten for Vacuum Apparatus<br>(V. N. Polyakov, V. P. Karshin, et al.; FIZIKO-KHIMICHESKAYA MEKHANIKA MATERIALOV, No 6, Nov-Dec 86)...              | 28 |
| Statistical Evaluation of Structural Characteristics and Hardening Obtained by Rolling Sintered Tungsten<br>(Ye. E. Z asimchuk, I. F. Zvorygin, et al.; POROSHKOVAYA METALLURGIYA, No 1, Jan 87)..... | 29 |
| Metallic Ag Powder Produced by Reduction of Ag Salt With Metol<br>(A. A. Ryabukha, O. V. Koleshova, et al.; POROSHKOVAYA METALLURGIYA, No 2, Feb 87).....                                             | 30 |

## NONMETALLIC MATERIALS

|                                                                                                                                                                         |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| New Generations of Ceramics<br>(Yu. D. Tretyakov; VESTNIK AKADEMII NAUKA SSSR, No 2, Feb 87).....                                                                       | 31 |
| Oxidation Resistance and Mechanical Strength of Hot-Pressed $Si_3N_4$ Ceramics<br>(Yu. G. Gogotsi, I. I. Osipova, et al.; POROSHKOVAYA METALLURGIYA, No 2, Feb 87)..... | 45 |

## PREPARATIONS

|                                                                                                                                                                                         |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Vitreous Metals<br>(A. Ya. Belenskiy; PRIRODA, No 2, Feb 87).....                                                                                                                       | 46 |
| Properties of Ni Modified by Implantation of Ag Ions<br>(I. S. Tashlykov, Ye. B. Boyko, et al.; FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86).....                           | 57 |
| Experimental Crystallization of Aluminum Melts in 'Evaporator-M' Apparatus<br>(V. N. Pimenov, V. F. Shulym, et al.; FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86).....       | 58 |
| Compensation of Marangoni Thermocapillary Effect During Directional Crystallization Under Microgravity<br>(V. N. Pimenov; FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86)..... | 60 |
| Effect of Plasma Arc Modulation on Adhesion and Gas-Permeability of Powder Coatings<br>(B. Ye. Gutman, M. Kh. Shorshorov; FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86)..... | 61 |

|                                                                                                                                                                                                          |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Effectiveness of Compacting Powders of BB-Cr15 Ball-Bearing Steel by Hot Extrusion<br>(Yu. L. Krasulin, N. V. Abashkina, et al.;<br>POROSHKOVAYA METALLURGIYA, No 1, Jan 87).....                        | 62 |
| Liquid-Phase Sintering of High-Density Compacts From Prepulverized Aluminum Alloys<br>(V. A. Vasilyev, B. S. Mitin, et al.; PROSHKOVAYA METALLURGIYA, No 1, Jan 87).....                                 | 63 |
| Structure of Hot-Pressed Materials Consisting of Sialon and Refractory Compound<br>(O. V. Bakun, O. N. Grigoryev, et al.; POROSHKOVAYA METALLURGIYA, No 1, Jan 87).....                                  | 64 |
| Effect of Laser Treatment on Structure and Composition of Plasma-Deposited Ni-Cr-Si-B Coatings<br>(V. P. Larionov, N. P. Bolotina, et al.; FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 1, Jan-Feb 87)..... | 65 |
| Composition of Fe-C and Al-Si Surface Layers After Contact With Plasma and Sputtering Products<br>(N. V. Popova, C. B. Bukelich, et al.; FIZIKI I KHIMIYA OBRABOTKI MATERIALOV, No 1, Jan-Feb 87).....   | 66 |
| Feasibility of Producing Fine-Disperse Composite Materials in Pulsed High-Enthalpy Stream<br>(I. V. Blinkov, A. G. Brodyagin, et al.; FIZIKA I KHIMKIYA OBRABOTKI MATERIALOV, No 1, Jan-Feb 87).....     | 67 |
| Production and Examination of Amorphous Zr Alloys<br>(I. A. Tregubov, L. N. Yevseyeva, et al.; FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 1, Jan-Feb 87).....                                             | 68 |
| Electrical-Contact Alloying of Steel Surface With Fibrous Carbon<br>(V. G. Syvynyuk, A. A. Zhukov, et al.; SVAROCHNOYE PROIZVODSTVO, No 2, Feb 87).....                                                  | 69 |
| Rate of Melting of Titanium in Melt of Stainless Steel<br>(V. A. Golubtsev, A. S. Noskov, et al.; IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA, No 2, Feb 87).....                      | 70 |
| Characteristics of Liquid-Phase Sintering of Mo-Cu Pseudoalloys With Biporous Structure<br>(L. I. Chernyshev; POROSHKOVAYA METALLURGIYA, No 2, Feb 87).....                                              | 71 |

|                                                                                                                                               |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----|
| Properties of Porous W-Cu and Mo-Cu Pseudoalloys<br>(A. V. Yegorov, A. G. Kostornov, et al.; POROSHKOVAYA<br>METALLURGIYA, No 2, Feb 87)..... | 72 |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Hardening Heat Treatment of Titanium Alloys With Rapid Heating<br>(A. I. Gordiyenko; METALLOVEDENIYE I TERMICHESKAYA<br>OBRABOTKA METALLOV, No 3, Mar 87)..... | 73 |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

## TREATMENTS

|                                                                                                                                                                             |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Electrical Properties of InAs After Bombardment by Fast Neutrons<br>(N. G. Kolin, V. B. Osvenskiy, et al.; FIZIKA I<br>KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86)..... | 74 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                                             |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Energy Losses by Reflection During Treatment of Materials With<br>High-Power Laser Radiation<br>(A. I. Skripchenko, V. N. Smirnov, et al.; FIZIKA I<br>KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86)..... | 76 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                                 |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Cross-Section for Formation of Recoil Atoms Under Bombardment<br>by 21 MeV Electrons<br>(V. P. Bababyev, M. G. Volkov, et al.; FIZIKA I KHIMIYA<br>OBRABOTKI MATERIALOV, No 6, Nov-Dec 86)..... | 78 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                           |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Deep Plasmochemical Etching of Si Through Double-Layer Masks<br>(M. V. Varlamov, V. Yu. Kireyev, et al.; FIZIKA I<br>KHIMIYA OBRABOTKI MATERIALOV, No 6, Nov-Dec 86)..... | 79 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                                                                   |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Effect of Refractory Elements on Relaxation Resistance of<br>High-Temperature Elinvar Alloys<br>(O. A. Khomenko, S. B. Mikhaylov, et al.; IZVESTIYA<br>VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA,<br>No 2, Feb 87)..... | 80 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                    |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------|----|
| High-Pressure Furnace for Sintering Refractory Compounds<br>(P. S. Kisliy, A. A. Shamray, et al.; POROSHKOVAYA<br>METALLURGIYA, No 2, Feb 87)..... | 81 |
|----------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                      |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Kinetics of $TiAl_3$ -Phase Formation in Ti-Al System<br>(V. N. Yeremenko, Ya. V. Natanzon, et al.; POROSHKOVAYA<br>METALLURGIYA, No 2, Feb 87)..... | 82 |
|------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                   |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Alloying by Laser Treatment<br>(L. S. Lyakhovich, S. A. Isakov, et al.; METALLOVEDENIYE<br>I TERMICHESKAYA OBRABOTKA METALLOV, No 3, Mar 87)..... | 83 |
|---------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                               |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----|
| Ways To Increase Erosion Resistance of Powder Steel<br>(P. A. Kulu; METALLOVEDENIYE I TERMICHESKAYA<br>OBRABOTKA METALLOV, No 3, Mar 87)..... | 84 |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                                              |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Effect of Heat Treatment and Thermochemical Treatment on<br>Properties of Hard Powder Alloys<br>(Yu. Yu. Pirso, Ya. P. Kyuvarsepp; METALLOVEDENIYE I<br>TERMICHESKAYA OBRABOTKA METALLOV, No 3, Mar 87)..... | 85 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                                                       |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Dependence of Phase Composition of VT23 Titanium Alloy on<br>Heating Temperature and Cooling Rate<br>(A. A. Il'in, M. Yu. Kollerov, et al.; METALLOVEDENIYE<br>I TERMICHESKAYA OBRABOTKA METALLOV, No 3, Mar 87)..... | 86 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

#### WELDING, BRAZING, SOLDERING

|                                                                                                                                                                                                                   |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Mechanical Characteristics of Welded Joints in Components of<br>VVER-1000 MW Water-Moderated Water-Cooled Power Reactors<br>(A. S. Zubchenko, S. I. Nosov, et al.; AVTOMATICHESKAYA<br>SVARKA, No 1, Jan 87)..... | 87 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                    |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Diffusion Welding of Mullite-Corundum Ceramics Through Copper<br>Interlayer<br>(R. A. Musin, Ya. V. Lyamin, et al.; AVTOMATICHESKAYA<br>SVARKA, No 1, Jan 87)..... | 88 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                                                                     |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Dependence of H <sub>2</sub> , C, N <sub>2</sub> , O <sub>2</sub> Distribution in Welded Joint<br>Produced Under Sea Water on Salinity of Latter<br>(O. D. Smiyan, V. Ya. Kononenko; AVTOMATICHESKAYA<br>SVARKA, No 1, Jan 87)..... | 89 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                         |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Formation of Front Wall of Metal Melting Channel During<br>Electron-Beam Welding<br>(V. Ya. Belenskiy; FIZIKA I KHIMIYA OBRABOTKA<br>MATERIALOV, No 1, Jan-Feb 87)..... | 90 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                                                      |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Diffusion Welding of CoNiTi16 Tungstenless Hard Alloy to<br>BBCr15 Ball-Bearing Steel<br>(G. A. Shchepetina, N. A. Mashkova, et al.;<br>SVAROCHNOYE PROIZVODSTVO, No 2, Feb 87)..... | 91 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|                                                                                                                                                  |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Reducing Residual Stresses in Welded Metal-Glass Joints<br>(V. A. Bachin, V. N. Gasteva, et al.; SVAROCHNOYE<br>PROIZVODSTVO, No 2, Feb 87)..... | 92 |
|--------------------------------------------------------------------------------------------------------------------------------------------------|----|

#### EXTRACTIVE METALLURGY, MINING

|                                                                                                |    |
|------------------------------------------------------------------------------------------------|----|
| The Scientific-Technical Revolution and Minerals<br>(L. V. Tauson; PRIRODA, No 2, Feb 87)..... | 93 |
|------------------------------------------------------------------------------------------------|----|

/12223



## ANALYSIS, TESTING

UDC 669.024.3.669.295:699.018.45

### KINETIC LAWS GOVERNING HIGH-TEMPERATURE OXIDATION OF INDUSTRIAL Ti ALLOYS

Kiev KIZIKO-KHIMICHESKAYA MEKHANIKA MATERIALOV in Russian Vol 22, No 6, Nov-Dec 86 (manuscript received 15 Jul 85) pp 76-80

[Article by G. G. Maksimovich, V. N. Fedirko and A. T. Lizun, Physical Mechanical Institute imeni G. V. Karpenko, UkSSR Academy of Sciences, Lvov]

[Abstract] An experimental study of VT1-0 titanium and eight Ti alloys, two binary ones (Ti+2.0% Al, Ti+5.0% Al) and six with additional  $\alpha$ -phase stabilizing elements (PT7M with 2.1% Al+2.5% Zr; OT4-1 with 1.7% Al+1.0% Mn; VT5-1 with 4.8% Al+2.5% Sn; VT6s with 5.1% Al+4.1% V; VT14 with 5.3% Al+3.3% Mo+1.1% V; VT23 with 5.5% Al+4.5% V+2.0% Mo+1.0% Cr+0.7% Fe) was made concerning the kinetics of their high-temperature oxidation and heat resistance in air at temperatures of 650-1000°C. Measurements before and after annealing of specimens were made by continuous weighing in a "Ugine Eyraud Setaram" B-70 thermoanalyzer, change of mass being plotted as a function of time at various temperatures in log-log coordinates so that the slope of the curves yielded the power-law exponent characterizing the mode of oxidation kinetics. Titanium VT1-0 and alloys Ti+2.0% Al, Ti+5.0% Al, OT4-1, VT6s, VT23 were found to oxidize according to a parabolic or almost parabolic law at 650°C and at 750°C, alloys PT7M and VT14 were found to oxidize slower than parabolically at 650°C but parabolically at 750°C and alloy VT14 was found to oxidize slower than parabolically at both 650°C and at 750°C. At higher temperatures of 850°C and 1000°C the oxidation of VT1-0 titanium and all eight alloys was found to become faster and closer to linear, because of cracking of the oxide layer, alloy VT14 still oxidizing slower than the others and thus having the highest heat resistance of all. The results indicate that only Al and Mo improve the oxidation resistance at temperatures of 650-1000°C, Zr improves it only at temperatures of 650-850°C, and Sn improves it only at temperatures of 650-750°C. References 15: 9 Russian, 6 Western.

2415/12223  
CSO: 1842/76



## FATIGUE FRACTURE OF RUNNER BLADES MADE OF HEAT-RESISTANT CAST Ni-Cr ALLOYS IN GAS-TURBINE ENGINES

Kiev PROBLEMY PROCHNOSTI in Russian No 1, Jan 87 (manuscript received 19 Feb 85) pp 46-50

[Article by I. A. Makovetskaya, O. I. Marusiy, B. A. Gryaznov and Yu. S. Nalimov, Strength Problems Institute, UkSSR Academy of Sciences]

[Abstract] Runner blades made of heat-resistant coarse-grain cast Ni-Cr alloys for gas-turbine engines were tested for fracture under a cyclic load. Three lots of blades were tested, one lot having been surface hardened by plastic deformation after casting, one lot having been annealed at a temperature of 1023 K for 6 h after casting and before surface hardening, one lot having been in service under real conditions in the first stage of an aircraft gas-turbine engine. Tests were performed in a P-646 electrodynamic vibration stand at a temperature of 973 K. The microstructure of the alloys after fracture was examined by the method of X-ray phase analysis in a DRON-2.0 diffractometer with a  $\text{CuK}_\alpha$  -radiation source and by the fractographic method under a "Necphot-2" optical microscope as well as under a "Stereoscan S4-10" electron microscope. Epigrams in "white" x-radiation from a Mo anticathode of a BSV-11 tube in a URS-2.0 camera yielded data on deformation and crystallographic orientation. Cracks were found to be initiated in the stable slip zone in a (111) plane, bounded by one of the largest grains, then propagates in the plane of maximum tensile stress with characteristic cyclic cleavage in one (100) plane and local shear in three (111) planes as well as formation of octahedral pits with plastic whiskers. The fatigue strength, on a 10 cycles base, and the fracture mode of tested new blades was found to depend on the surface treatment and almost not at all on the overall heat treatment, the fracture being intragranular. While a blade operates under real service conditions, its case develops a fine-grain structure and detrimental impurities then segregate at grain boundaries, which facilitates cracking by the intergranular mechanism during subsequent laboratory testing. References 18: 5 Russian, 13 Western (2 in Russian translation).

2415/12223  
CSO: 1842/77

TEMPERATURE AND ORIENTATION DEPENDENCE OF MOMENTARY STRENGTH CHARACTERISTICS, YOUNG'S MODULUS, AND LINEAR EXPANSIVITY OF SINGLE CRYSTALS OF ZhS6F HEAT-RESISTANT ALLOY

Kiev PROBLEMY PROCHNOSTI in Russian No 1, Jan 87 (manuscript received 14 Aug 84) pp 51-56

[Article by I. L. Svetlov, N. N. Sukhanov, A. I. Krivko, I. N. Roshchina, I. M. Khatsinskaya and A. I. Samoylov, All-Union Aviation Materials Scientific Research Institute, Moscow]

[Abstract] An experimental study of single crystals of the ZhS6F heat-resistant alloy was made for the purpose of determining the temperature and orientation dependence of their momentary strength characteristics, their Young's modulus, and their temperature coefficient of linear expansion. Ingots 20 mm in diameter and 150-180 mm long were grown by the Petrov-Tumanov method (U.S. Patent No 3,857,436) with appropriate seeds, four batches of them with  $\langle 100 \rangle$ ,  $\langle 011 \rangle$ ,  $\langle 111 \rangle$ ,  $\langle 112 \rangle$  orientations respectively. Some of each were tested as cast, others were tested after heat treatment consisting of homogenization at 1235°C in a vacuum furnace for 1 h and subsequent cooling in an argon atmosphere at rates of 50-80°C/min. Mechanical characteristics, namely 0.2%-set yield strength, critical shear strength, ultimate tensile strength, and percentage elongation, were measured in an "Instron" machine at temperatures of 20-950°C under a deformation rate of 0.1 cm/min. The static modulus of elasticity at room temperature was calculated from stress-strain curves which had been plotted with an extensometer. The dynamic modulus of elasticity at 20-800°C was measured in an "Elastomat" machine. The temperature coefficient of linear expansion was measured in a "Lincise" dilatometer. Crystal orientation and lattice rotation were monitored in a DRON-3.0 X-ray diffractometer. The results of these tests and subsequent fractographic analysis reveal a pronounced anisotropy of all strength characteristics up to 900°C, single crystals with  $\langle 111 \rangle$  orientation remaining strongest

and single crystals with  $\langle 011 \rangle$  orientation remaining weakest, whereupon they become isotropic at  $950^{\circ}\text{C}$ . The maximum static and dynamic moduli of elasticity have single crystals with  $\langle 001 \rangle$  orientation. The minimum static and dynamic moduli of elasticity have single crystals with  $\langle 111 \rangle$  orientation. The anisotropy of both moduli vanishes at  $800^{\circ}\text{C}$ . The temperature coefficient of linear expansion is isotropic throughout the temperature range and the same for single crystal of all orientations, equal to that for an equiaxial alloy crystal. References 10: 3 Russian, 7 Western (2 in Russian translations).

2415/12223

CSO: 1842/77

## CHANGES IN MECHANICAL CHARACTERISTICS OF MOLYBDENUM CAUSED BY THERMOCHEMICAL TREATMENT

Kiev PROBLEMY PROCHNOSTI in Russian No 1, Jan 87 (manuscript received 28 Jan 85) pp 95-97

[Article by L. P. Skuratov, V. K. Yatsimirskiy and N. V. Kirilova, Kiev University]

[Abstract] An experimental study of molybdenum and its treatment with  $N_2$  or  $NH_3$  at high temperatures was made for the purpose of determining the interaction and its effect on the mechanical characteristics. Specimens were treated in a reactor chamber first at  $20^\circ C$  in air, which was then expelled by a stream of working gas ( $Ar$ ,  $NH_3$ ,  $N_2+H_2$  mixture,  $N_2+H_2+NH_3$  mixture), then heated in that gas to  $6000^\circ C$  within 3 min, held at that temperature for 30 min, then heated to  $1000^\circ C$  within 2 min, and tested for creep till fracture at that temperature. Metallographic examination revealed a brittle fracture and no visible surface impregnation zones. Both surface and bulk microhardness were found to have increased, treatment in  $N_2+H_2$  mixture being most effective. The surface of specimens became covered with a sooty tarnish which included a violet streak during treatment in air and covered with a dull-gray film during treatment in  $N_2+H_2$  or  $N_2+H_2+NH_3$ , but remained almost clean during treatment in  $NH_3$  alone. Chemical and thermodynamic analysis revealed formation of  $Mo_2N$  over a wide range of reaction temperatures, a major factor causing changes in the mechanical characteristics. Addition of  $NH_3$  to  $N_2+H_2$  mixture had increased the rate of deformation and decreased the ultimate strength, with increasing  $NH_3$  concentration, a mixture with 33.3%  $NH_3$  having the same unfavorable effect as pure  $NH_3$ . References 5: all Russian.

2415/12223  
CSO: 1842/77

ACOUSTICAL CHARACTERISTICS OF INVAR POWDER ALLOYS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87 (manuscript received 21 Jan 86) pp 95-98

[Article by V. A. Vershinin, V. I. Kostikov, V. A. Belyanin, Yu. F. Maksimov, K.P.:. Mikonov and N. D. Pautkov, Yoshkar-Ola]

[Abstract] An experimental study of two Invar powder alloys, 36Ni and 32NiCoCu, was made for a determination of the temperature dependence of their Young's modulus, shear modulus, Poisson's ratio, and acoustic characteristics represented by the velocity of longitudinal sound waves. Measurements were made by the method of resonance vibrations, using disks 4 mm thick and 17 mm in diameter produced by pressing in rigid metal molds and sintering at 1250°C for 2 h in an atmosphere of dissociated NH<sub>3</sub>. Specimens with different residual porosity were thus produced, that of the 36Ni alloy ranging from 4.4% to 18.5% and that of the 32NiCoCu alloy ranging from 3.6% to 15.0%. Measurements were made at temperatures from +30°C to -100°C, in an atmosphere of gaseous nitrogen under normal pressure. the results reveal Invar characteristics of these alloys: a monotonic increase of both moduli and the acoustic velocity with rising temperature and an attendant monotonic decrease of the Poisson's ratio. They also reveal a dependence of the acoustic velocity as well as of both moduli on the residual porosity, with the maxima corresponding to 4.4% or 3.6% porosity, depending on the temperature, and the maximum Poisson's ratio corresponding to 3.5% porosity throughout the entire temperature range. References 9: all Russian.

2415/12223  
CSO: 1842/78



UDC 539.216:546.663.535.34:537.226

OPTICAL CHARACTERISTICS OF  $Y_2O_3$ - $Eu_2O_3$  FILMS PRODUCED BY ION BOMBARDMENT OF HOT-PRESSED TARGETS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87  
(manuscript received 24 Feb 86) pp 98-100

[Article by A. F. Andreyeva, M. A. Katsitadze and N. G. Khatynenko, Institute of Materials Science Problems, UkSSR Academy of Sciences]

[Abstract] An experimental study of  $Y_2O_3$  films doped with Eu was made for a determination of their optical characteristics, such 200  $\mu m$  thick films having been deposited on sapphire single crystals at a condensation temperature of 800°C by ion bombardment of hot-pressed oxide targets. Their composition was determined in a "Kameka-MS" microanalyzer and their structure was examined with an EG-100 electron-diffraction reflex camera. The results reveal a linear dependence of the lattice period on the Eu O concentration over the entire 0-100%  $Eu_2O_3$  range. Transmission and reflection of light were measured with "Specord UV-Vis" and "UR-20" spectrophotometers, whereupon the respective coefficients and the absorption coefficient as well were calculated taking into account multiple reflections. The spectral characteristics indicate a 90-95% transparence of all films to all visible light, with an absorption coefficient which increases with increasing  $Eu_2O_3$  concentration while the edge of the fundamental absorption band shifts linearly toward shorter wavelengths. The energy gap was calculated by extrapolating the linear segment of the dependence of the absorption coefficient squared on the energy of incident photons, while yielded an energy gap decreasing linearly from 5.8 eV for pure  $Y_2O_3$  to either 4.9 eV for pure B- $Eu_2O_3$  or 4.48 eV for pure C- $Eu_2O_3$  depending on which of the two linear segments found to exist for  $Eu_2O_3$  was extrapolated. References 5: 4 Russian, 1 Western.

2415/12223  
CSO: 1842/78

## DEFECTOSCOPIC CHARACTERISTICS OF SMALL BETATRON MIB-4

Sverdlovsk DEFECTOSKOPIYA in Russian No 1, Jan 87 (manuscript received 27 Nov 85) pp 27-31

[Article by D. A. Boyko, A. A. Filimonov, and V. L. Chakhlov, Electron Introscopy Scientific Research Institute, Tomsk]

[Abstract] A small betatron operating in the pulse mode with 4 MeV electrons has been developed for inspection of reinforced-concrete structures, welded joints, assemblies, and materials. It consists of a radiation source, a generator of current pulses, and a control panel. Current pulses with a repetition rate up to 200 Hz energize the emitter electromagnet and bremsstrahlung is generated with an intensity of at least 1.0 R/(m.min). Its design and performance are analyzed on the basis of experimental inspection of steel strips using various shields (pb1.0, Fe1.0, Ta1.0), or none, and various X-ray films (D5 and D7 made in Belgium, NDT-55 and NDT-65 made by Dupont, TF-12 and TF-13 made by ORWO in East Germany). The bremsstrahlung dose must be increased and the absolute sensitivity decreases with increasing thickness of the inspection piece, such as steel strip. Both diffuseness and minimum focal length, but not density, of x-radiograms increase with increasing thickness of the inspection piece. The performance of this MIB-4 betatron is comparable with that of a 15 MeV betatron and betatrons using  $^{60}\text{Co}$  or  $^{192}\text{Ir}$  radiation sources. The authors thank Yu. A. Samoryanov and A. V. Ivanov of the Ministry of Foreign Trade, also Dr Eng A. Heidemann of the Hannover University, N. Riess, president of "Helling" GmbH in Hamburg/FRG and Prof A. Honnig at its Center of Radiation Defectoscopy. References 4: 2 Russian, 2 Western.

2415/12223  
CSO: 1842/81

UDC 62-987:621.762

TUNGSTENLESS HARD ALLOY ON TiC BASE PRODUCED BY VARIOUS METHODS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87  
(manuscript received 25 Jul 85) pp 101-103

[Article by V. K. Vitryanyuk, A. F. Kolchik, E. S. Simkin, S. I. Sklyar and N. V. Tsypin, Superhard Materials Institute, UkSSR Academy of Sciences]

[Abstract] An experimental study of the TiNi<sub>20</sub> tungstenless carbide alloy hot pressed by various methods was made for a comparative evaluation of these methods and also for optimization of the composite material combining this alloy with synthetic AS32-400/315 diamond crystals. Alloy powder was hot pressed in graphite molds under vacuum, in air, or under high pressure within or near the range of diamond's thermodynamic stability. A batch of the alloy was also produced by the industrial "free" sintering under vacuum. Respective specimens of this alloy were then tested by standard methods for density and hardness and also for abrasive wear by white electrocorundum 100/80 powder. The highest wear resistance was found to have the alloy sintered under high pressure, with 89% of grains within the 0.5-1.5  $\mu$ m fraction and 11% of them within the 1.5-2.5  $\mu$ m fraction. The alloy thus produced therefore is most suitable for combining with diamond crystals. This has been confirmed by the performance of PP 600x63x300 mm 24A24SM25K6 grinding wheels, comparable to that of wheels dressed with Tvesal combining diamond crystals with a tungsten alloy. References 11: all Russian.

2415/12223

CSO: 1842/78

# INDUCED RADIOACTIVITY OF STEEL PARTS DURING INDUSTRIAL DEFECTOSCOPY WITH ELECTRON ACCELERATORS

Sverdlovsk DEFECTOSKOPIYA in Russian No 1, Jan 87 (manuscript received 12 Aug 85, in final version 2 Jul 86) pp 36-43

[Article by V. V. Varnavskiy and P. P. Zolnikov, Sverdlovsk Institute of Engineering Education]

[Abstract] An experimental study of industrial defectoscopy with betatron electron accelerators was made for the purpose of determining the induced radioactivity of various steels and structural betatron components. Only activation by photoneutron reactions was considered, the cross-sections for all other photonuclear reactions being much smaller. Specimens of six carbon steels (St3, ST20, St30, St35, St25 cast, St35 cast) and five alloy steels (10CrNiSiCu, 09Mn2Si, 110Mn13 cast, 14Cr2MnMoB cast, 12Cr18Ni10Ti) were tested with betatrons B5D-25 and B-35/8 and the contributions of isotopes  $^{53}\text{Fe}$ ,  $^{62}\text{Cu}$ ,  $^{11}\text{C}$ ,  $^{49}\text{Cr}$ ,  $^{57}\text{Ni}$ ,  $^{92}\text{Mo}$ ,  $^{179}\text{W}$  to the total radioactivity were determined, these isotopes known to be the major contributors. The data, evaluated according to applicable formulas, have yielded the energy spectrum of induced  $\gamma$ -radiation and the dependence of its dose power at the surface of an inspection piece or of the betatron on the length of exposure time, on the thickness of a steel specimen or a betatron part, on the intensity of incident bremsstrahlung, and on the time after exposure. The results indicate that isotopes  $^{52}\text{Fe}$  and  $^{62}\text{Cu}$  are the principal contributors to induced radioactivity of steels and betatron parts respectively, more than 90% of it appearing in the form of  $\gamma$ -radiation with three peaks (0.14, 0.38, 0.51 MeV) within its 0-0.7 MeV energy spectrum. The power of this radiation increases with increasing exposure time for steels, saturating after 40 min, with increasing thickness of steel samples up to approximately 42 mm, and linearly with increasing intensity of incident bremsstrahlung. During industrial inspection the induced radioactivity can well exceed its maximum permissible level of 0.2 pC/kg.s and requires special safety measures. References 9: all Russian.

UDC 66.094.1:621.745.5

**ANALYSIS OF SMELTING PROCESSES FOR REDUCTION OF TITANIUM-MAGNETITE ORE PELLETS**

Moscow IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA in Russian No 2, Feb 87 (manuscript received 19 Jun 85) pp 7-10

[Article by Yu. A. Deryabin and Yu. S. Shchekalev, Ural Scientific Research Institute of Ferrous Metals, Sverdlovsk]

[Abstract] The process of reducing titanium-magnetite ores with a high vanadium content (58% Fe, 3.00-12.00%  $TiO_2$ , 0.50-1.16%  $V_2O_3$ , 2.40-3.50%  $Al_2O_3$ , 1.90-3.70% SiO, 1.90-3.70% CaO, 1.40-3.00% MgO, 0.25-0.40% MnO) from three deposits (Kachkanar, Kopanskoye, Chineyskoye) by smelting pellets of these ores at 1600°C is analyzed on the basis of data on their chemical composition and computer-aided simulation of reduction-smelting thermodynamics. Calculations made on a YeS-1020 computer, taking into account material balance as well as heat balance, indicate that the peak on the vanadium-carbon equilibrium diagram shifts toward a higher than 2-3% C content and that the Si content can, depending on the rate of FeO reduction, monotonically decrease, monotonically increase, or first decrease to a minimum and then increase. The results are comparable with those pertaining to reduction of titanium-magnetite ores from the Bushveld deposit (South Africa), which contain 56-58% Fe and 1.3%  $V_2O_3$  in addition to 12-14%  $TiO_2$ . References 6: 5 Russian, 1 Western.

2415/12223

CSO: 1842/94



UDC 621.785

## SUCCESSIVE BORON-CHROMIUM IMPREGNATION OF CARBON STEELS

Kiev FIZIKO-KHIMICHESKAYA MEKhanika MATERIALOV in Russian Vol 22, No 6, Nov-Dec 86 (manuscript received 23 Dec 85) pp 24-26

[Article by V. D. Kalner, M. G. Karpman and S. D. Kulazhenkov, Moscow Automobile Plant imeni I. A. Likhachev]

[Abstract] A study was made concerning successive boron-chromium impregnation of carbon steels, looking toward development of a technology which will inhibit deboronization of the boride layers, deboronization having been found to be caused by interaction of FeB and Fe<sub>2</sub>B with atmospheric oxygen or with bound oxygen in the processing medium such as H<sub>2</sub>O or CO<sub>2</sub>. Specimens of 08 killed carbon steel and U8A carbon steel were first boron impregnated by the contact method with a mixture of B<sub>4</sub>C<sub>3</sub> powder and NaF activator in containers with "fusible plug," in a gaseous medium. They were then chromium impregnated by the contactless method with 1-5 mm large lumps of grade-0 chromium in a vacuum furnace under a pressure of 1.33 Pa with injection of CCl<sub>4</sub> vapor into the reaction zone during heating. The distributions of carbon and boron across the surface layer were determined on the basis of activation analysis; the distributions of Fe and Cr across the surface layer were determined on the basis of metallographic analysis. The results indicate that during boron impregnation of U8A steel carbon is driven from the boride zone toward its boundary, where it forms carboborides, the thickness of the carboboride zone as well as that of the boride zone then increasing during subsequent chromium impregnation. This technology has been found to yield a nondefective diffusion layer with a protective surface whose structure does not depend on the thickness of the boride layer underneath and on the carbon content in the steel. Experimental tools dies and engine pistons with such boron-chromium impregnation were tested under normal operating conditions and found to have a 2-3 times longer life than conventionally heat treated ones. References 9: 7 Russian, 1 Polish, 1 Western.

2415/12223  
CSO: 1842/76

## COMBINED CORROSIVE AND FRICTIONAL WEAR OF MEDIUM-CARBON STEEL WITH EUTECTIC COATINGS IN SALT SOLUTION

Kiev FIZIKO-KHIMICHESKAYA MEKhanika MATERIALOV in Russian Vol 22, No 6, Nov-Dec 86 (manuscript received 29 Jul 87) pp 27-30

[Article by V. M. Golubets, G. A. Preys, A. G. Dzyub, M. I. Pashenko and Yu. G. Sukhenko, Physical Mechanical Institute imeni G. V. Karpenko, UkSSR Academy of Sciences, Lvov]

[Abstract] A study of eutectic coatings of St45 carbon steel was made for a determination of their wear resistance under mechanical friction in a corrosive 3% aqueous NaCl solution. Four coatings were tested: 1)  $\alpha$ -Fe + Fe<sub>0.4</sub>Mn<sub>3.6</sub>C + Fe<sub>3</sub>C + Fe<sub>2</sub>B; 2)  $\gamma$ -(Fe,Ni) + Fe<sub>0.4</sub>Mn<sub>3.6</sub>C + Fe<sub>3</sub>C; 3)  $\delta$ -(Fe,Cr) + Fe<sub>0.4</sub>Mn<sub>3.6</sub>C + Fe<sub>3</sub>C; 4)  $\delta$ -(Fe,Ni,Mn) +  $\alpha$ -(Fe,Cr) + Fe<sub>0.4</sub>Mn<sub>3.6</sub>C + Fe<sub>3</sub>C. They were tested in face friction against a 24A25NSM16K5B grinding wheel, with surface finishing of the metal electrode, at a sliding velocity of 0.8 m/s under a load pressure of 0.35, 0.70, 1.40 MPa. The electrode potential of the coatings was measured under stationary conditions, during friction, and during abrasion under the highest negative friction potential at the beginning of wear. Polarization curves were plotted by the potentiostatic method with an AgCl reference electrode, with the potential swept from cathode to anode at a rate of 0.5 mV/s beginning at a level of -0.9...-1.1 V. The wear was measured by the gravimetric method with an error not exceeding 0.0002 g after 30 minutes. Abrasive wear was found to cause a negative shift of the stationary potential,, while increasing the load pressure was found to accelerate anodic processes with attendant shifting of the anodic polarization curves toward higher current density much more than cathodic processes. The pressure dependence of the corrosion rate under mechanical friction was evaluated on the basis of the autodissolution current, by extrapolation of potentiodynamic curves plotted at low sweep rates. the coatings can be ranked in the order (1), (2), (4), (3) with respect to increasing autodissolution current and in the order (3), (1), (2), (4) with respect to increasing wear. Coating (3) has the highest wear resistance in absence of external polarization. Cathodic polarization decreases the wear of coating (1) as the current density is increased from 30 A/m to 38 A/m.

Anodic polarization decreases the wear of coatings (2) and (4) as the current density is increased from 30 A/m<sup>2</sup> to 38 A/m<sup>2</sup> .  
References 6: all Russian.

2415/12223  
CSO: 1842/76

## PLASMA METALLIZATION OF REFRACTORY CARBIDE POWDERS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6,  
Nov-Dec 86 (manuscript received 2 Sep 85) pp 57-60

[Article by Ye. B. Koroleva, N. A. Klinskaya, O. F. Rybalko and  
T. A. Ugolnikova, Moscow and Sverdlovsk]

[Abstract] Metallization of refractory carbide powders by cold plasma treatment was studied in an experiment for an evaluation of this process in terms of effectiveness and resulting powder characteristics. Nickel powder with grains smaller than  $6\text{ }\mu\text{m}$  was used for plating  $\text{TiC}$ ,  $\text{WC}$ ,  $\text{Cr}_3\text{C}_2$  powders with grains within the  $40\text{-}80\text{ }\mu\text{m}$  size fraction, such carbide powders being most suitable for coating other materials from the gaseous phase. Plating was done with a segmented plasmatron using argon as both plasma generating and powder transporting gas, powder being fed to the hermetic process chamber in state of suspension. The effectiveness of this process was evaluated by the method of magnetic separation and measuring the yield of magnetic particles. The yield of spherical particles was determined under an optical microscope, the size distribution of powder grains after treatment was determined on the basis of sieve analysis, and the change in their composition was determined on the basis of chemical analysis and X-ray phase analysis in an DRF-2.0 diffractometer with filtered Co-line radiation. powder of each carbide was thus tested for decarbonization, loss of free carbon and loss of bound carbon, in the process of prespheroidization, spheroidization after saturation plating with 30% Ni, and subsequent granulation. The authors thank V. A. Petrunichev and L. V. Solovyev for analysis of the results and valuable comments. References 5: all Russian.

2415/12223  
CSO: 1842/82

AIR PLASMATRON PNV-23 FOR DEPOSITION OF COATINGS

Kiev AVTOMATICHESKAYA SVARKA in Russian No 1, Jan 87 (manuscript received 16 May 85, in final version 16 Jul 86) pp 73-74

[Article by M. V. Karasev, candidate of technical sciences, V. S. Klubnikin, candidate of technical sciences, and G. K. Petrov, candidate of technical sciences, Leningrad Polytechnical Institute imeni M. I. Kalinin]

[Abstract] A new plasmatron PNV-23 with air as plasma generating gas has been developed for deposition of metal powder coatings. This machine, with a power rating of 60 kW, has a thermochemically treated Hf cathode and interelectrode inserts. Air is injected at a rate of 0.8-1.5 g/s tangentially on the cathode side and powder is fed into the dead zone of the plasma stream. A current of 100-300 A, generated by a voltage of 175-200 V, ensures adequate thermal power of the plasma stream. The efficiency reaches 50-75%, depending on the air rate. The plasmatron was tested with PG-SR3 powder (0.85% C, 15.35% Cr, 1.64% Fe, 2.87% Si, 0.004% O<sub>2</sub>) as well as PN-85Al15, PN-55Ti45, and Al<sub>2</sub>O<sub>3</sub> powders on St40 carbon steel. The coatings were analyzed for oxygen content and loss of alloying elements as well as for adhesion strength. The results indicate that the adhesion strength increases with decreasing distance from nozzle throat to coated surface and with increasing travel speed of the coated part under the nozzle, while the porosity decreases but the oxygen content increases with decreasing powder grain size. The performance of this plasmatron is on par with that of the PN-21 argon plasmatron, but provides for wider control of the powder grain size and produces thicker corundum coatings. References 1: Russian.

2415/12223

CSO: 1842/79



DEPOSITION OF COATINGS OF SELF-FLUXING ALLOY BY MEANS OF GAS-AIR PLASMA

Kiev AVTOMATICHESKAYA SVARKA in Russian No 1, Jan 87 (manuscript received 29 Oct 85, in final version 17 Jul 86) pp 74-75

[Article by D. A. Demchuk, candidate of technical sciences, S. Ya. Shekhter, candidate of technical sciences, and L. M. Yezhikova, engineer, Donetsk Scientific Research Institute of Ferrous Metallurgy]

[Abstract] Coatings of the PG-10N-01 self-fluxing alloy powder were experimentally deposited on steel specimens with the "Ukraine" plasmatron using air as oxidizer, gaseous shield and transport medium, this machine having a water-cooled Cu cathode with a cylindrical Zn insert. The powder was fed to the main anode while air mixed with propane-butane gas was fed under the intermediate anode. The optimum feed rates were found to be 2.7 m<sup>3</sup>/h air for shielding the cathode, 12.4 m<sup>3</sup>/h air for mixing with 2.4 m<sup>3</sup>/h propane-butane gas, and 0.4 m<sup>3</sup>/h air for transporting the powder. With a steady-state current of 240 A, which produces a 320-330 V drop across the arc, and a 180-200 mm distance from nozzle throat to coated surface, the machine was found to deposit powder at a rate of 20 kg/h. The powder was fused into a coating after a 2-2.5 mm thick layer had been deposited. The results of mechanical tests and metallographic examination under a "Neophot-2" microscope indicate that the adhesion is strongest when coatings have been deposited in an air(oxygen)-deficient medium, but that too much deficiency destabilizes the plasmatron. With less than 60% theoretical air the coating thickness becomes nonuniform and, while the adhesion remains strong, the coatings become defective because of weakening cohesion. Fusion of the powder results in appearance of a diffusion zone with a distinct boundary between softer coating and harder base metal. References 3: all Russian.

2415/12223  
CSO: 1842/79

UDC 621.791.92:621.791.72:621.373.826

## INCREASING PRODUCTIVITY AND SCOPE OF LASER HARDFACING

Moscow SVAROCHNOYE PROIZVODSTVO in Russian No 2, Feb 87 pp 1-4

[Article by N. N. Odintsov, engineer, L. A. Shternin, candidate of technical sciences, V. S. Smirnov, candidate of technical sciences, and S. K. Kartavyy, engineer, All-Union Electric Welding Equipment Scientific Research Institute Equipment]

[Abstract] Laser hardfacing with the material fed directly into the interaction space in the process is analyzed for ways to increase the productivity and the scope so as to ensure most economical utilization of costly power lasers, this method being already preferable to hardfacing with the material in foil, ribbon, wire, powder, or other form predeposited on the treated surface. Experimental data on hardfacing copper and polymethyl methacrylate, including macrostructural examination, combined with calculation of the hardfacing geometry and the radiation power density distribution indicate that hardfacing with a scanning laser and with simultaneous feed of powder is most productive and controllable. A power density distribution less than 18% nonuniform will yield a wider and better layer per pass, if it is varied according to the law most appropriate for a given application. Equipment has been developed on this basis for hardfacing with tungsten alloy VSNGN35 powder or nickel alloy PGSR4 powder. References 10: 6 Russian, 4 Western.

2415/12223

CSO: 1842/80

**STRUCTURE AND PROPERTIES OF ANTICORROSIVE WEAR-RESISTANT COATINGS  
PRODUCED BY PLASMA HARDFACING WITH POWDER MATERIALS**

Moscow SVAROCHNOYE PROIZVODSTVO in Russian No 2, Feb 87 pp 4-5

[Article by E. S. Komarcheva, candidate of technical sciences, L. G. Mishchenko, engineer, and S. S. Salkova, candidate of technical sciences, All-Union Electric Welding Equipment and Scientific Research Institute, V. B. Mordynskiy, candidate of technical sciences, All-Union Scientific Research Institute of Petroleum Machine-Building]

[Abstract] An experimental study of plasma hardfacing of petrochemical-grade alloy steels 40Cr and 45Cr5 with self-fluxing powder materials was made, its purpose being to determine the structurization and the properties of deposited layers. Corrosion- and wear-resistant nickel alloy powders PGSR2/3/4 were used for hardfacing specimens of those steels with the UPN-303 plasmatron built at the Electric Welding Equipment Scientific Research Institute. Hardfacing was done at rates of 6-11 m/h, with the arc current of either polarity varied over the 100-145 A range and the powder feed rate varied over the 2-3.2 kg/h range. The plasmatron oscillation amplitude and frequency were 15 mm and 0.25 Hz respectively. Argon was used as the plasma generating gas at a rate of 50 l/h, and also as powder transporting gas and cathode shielding gas at a rate of 900-1000 l/h each. The distance from plasmatron to steel specimen was 10-15 mm. Either one layer or two layers were deposited, tested for hardness, and metallographically examined for macrostructural characteristics. The results indicate a wide range of controllability and ways to optimize such coatings for maximum hardness and wear resistance.

2415/12223  
CSO: 1842/80

PLASMA-DEPOSITED TiC COATINGS

Moscow SVAROCHNOYE PROIZVODSTVO in Russian No 2, Feb 87 pp 11-12

[Article by V. B. Raytses, engineer, V. M. Litvin, engineer, V.P. Rutberg, engineer, and G. P. Kalashnikov, engineer, Zaporozhye Industrial Institute]

[Abstract] An experimental study of plasma deposition of TiC coatings was made where TiC powder had been nickel-plated to ensure satisfactory precipitation and adhesion. Plain TiC powder had been plated by sedimentation of Ni from a  $\text{NiCl}_2$  electrolyte, the 40-60  $\mu\text{m}$  large plated particles containing 55% Ti, 14% C, 30.5% Ni, and only 0.5% impurities. This powder was used for depositing 0.8-1.0 mm thick coatings on specimens of St45 carbon steel with a GN-5R plasmatron, after the steel surface had been ground and sand-blasted. For optimization of such coatings in terms of wear resistance, eight experiments were performed according to a 4-factor 3-level matrix plan with arc current, powder feed rate, surface scan rate, and coating thickness varied. Wear resistance was measured in an MI-1 friction machine; that of nickel-plated TiC coatings was found to be 3-3.5 times higher than that of U8 carbon tool steel.

2415/12223

CSO: 1842/80



UDC 620.179.163

NONDESTRUCTIVE METHOD OF DETERMINING CRITICAL LOADS FOR BEAMS,  
PLATES, AND SHELLS MADE OF COMPOSITE MATERIALS

Kiev PROBLEMY PROCHNOSTI in Russian No 1, Jan 87 (manuscript  
received 30 May 85) pp 80-84

[Article by V. P. Georgiyevskiy and I. S. Malyutin, Moscow]

[Abstract] A variant of the resonance method is proposed for determination of critical loads for structural elements, especially thin ones, made of composite materials. It is based on a functional dependence of the critical load on the frequency of natural vibrations and on the wave formation pattern prior to loss of stability. This relation involves neither the elastic characteristics of the material, which therefore need not be determined, nor the degree of its anisotropy and does not depend on the mode of loading. It is derived from the differential equation of flexural vibration. When the corresponding problem of stability can be solved explicitly, as in the case of a simple beam with uniform cross-section, then only a regression analysis is necessary for determining the stiffness coefficients from geometrical dimensions and masses. When the problem of stability can only be solved implicitly, as in the case of more intricate shapes and constraints other than hinge support, then  $r$  tests are required for determining the frequencies and the modes of natural vibrations before numerical methods of solution are applied. A practical implementation of this method is demonstrated on plates and cylindrical shells made of a plastic material with an orthogonal pattern of glass-fiber reinforcement. References 8: 7 Russian, 1 Western (in Russian translation).

2415/12223  
CSO: 1842/77

UDC 620.172.241.224:678.5-419.8

RESISTANCE OF POLYMER COMPOSITE MATERIALS TO INTERLAMINAR SHEAR  
AT HIGH TEMPERATURES

Kiev PROBLEMY PROCHNOSTI in Russian No 1, Jan 87 (manuscript  
received 9 Jan 86) pp 84-89

[Article by A. V. Kudryavtsev, Strength Problems Institute, UkSSR  
Academy of Sciences, Kiev]

[Abstract] A methodology has been developed for experimentally determining the resistance of polymer composite materials to interlaminar shear not only at room temperature but also at high temperatures up to 2273 K. The simplicity of a short bar is combined with transverse grooves so as to ensure minimum thickness in the neutral plane, where normal stresses are zero and shearing stresses are maximum. Two necessary conditions for high-temperature testing are satisfied, namely attainment of a given state of stress in the specimen and a uniform temperature distribution over its cross-section. This is achieved by notches cut precisely within the gage segment and by automatic heating at a program-controlled rate, with thermal insulation around the end segment of the specimen minimizing leakage of heat through the clamps. Bars of a carbon-plastic material were tested according to this scheme. The results indicate that, as the temperature rises, adhesion and cohesion of the polymer binder decrease faster than the tensile strength of filler monolayers, which causes rupture in shear to occur within the notched segment and in only one plane here. References 15: 9 Russian, 6 Western.

2415/12223

CSO: 1842/77

UDC 669.71+621.721:539.373

**MODELING COMPACTION PROCESS FOR PRODUCTION OF FIBROUS COMPOSITE MATERIALS**

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 1, Jan-Feb 87 (manuscript received 21 Nov 85) pp 119-123

[Article] Based on a model of the compaction-by-rolling process for production of fibrous composite materials, a program has been developed for computer-aided calculation and optimization of the process parameters. The process involves simultaneous compression of a structurally nonhomogeneous porous plastic binder and bonding it to brittle high-strength reinforcement fibers by rolling parallel to the latter. The process must ensure not only maximum density and minimum porosity of the compact, as well as complete continuity of fibers and thus the required load capacity, but also the bond strength required for a given mode of fracture under given overloading conditions. The algorithm covers stacking for rolling and deformation during rolling, with only the six most significant influencing factors taken into account. These are volume fraction of fibers, initial tensile strength of fibers, horizontal pitch of reinforcement pattern, radius of rollers, rolling speed, and final thickness of composite material. The model was verified by a numerical experiment and mechanical testing of physical specimens with only four of those factors varied, its adequacy having been found not to depend on the initial tensile strength of fibers and on the horizontal pitch of the reinforcement pattern. References 2: both Russian.

2415/12223  
CSO: 1842/93

## COMPOSITE MATERIALS BASED ON HYDROGEN-ABSORBING INTERMETALLIC COMPOUNDS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 28 Oct 85) pp 59-63

[Article by M. M. Antonova, T. I. Brataninch, S. N. Yendrzheyskaya, I. I. Karpikov, V. S. Lukyanchikov, I. F. Martynova, V. V. Skorokhod, S. M. Solonin and I. M. Shalya, Institute of Materials Science Problems, UkSSR Academy of Sciences]

[Abstract] An experimental study was made concerning the production and performance characteristics of composite materials for automotive hydrogen storage batteries based on intermetallic compounds absorbing hydrogen at room temperature. Four such materials, namely  $Ti_2Ni + 37\% Ni$ ,  $TiFe + 57\% Ni$ ,  $LaNi_5 + 50\% Ni$  and  $LaNi_5 + 50\% Cu$ , were produced from powder mixtures by sintering and then hydrogenated under pressure up to saturation. The hydrogen concentration was measured by the desorption method. Hydrogenation of the  $Ti_2Ni + 37\% Ni$  composite, containing also a  $TiNi$  phase, and of the  $Ti_2Ni$  compound alone was first done under a pressure of 0.1 MPa, for determination of the temperature dependence of their absorption capacity and the dependence of their relative volume change on the concentration of absorbed hydrogen. The results indicate that the relative volume change increases appreciably with increasing  $H_2$  concentration. The absorption capacity of both  $Ti_2Ni$  and  $Ti_2Ni + 37\% Ni$  was found to be approximately the same (below 100  $cm^3/g$ ) at 400-450°C, but that of  $Ti_2Ni + 37\% Ni$  to be much higher (200  $cm^3/g$ ) than that of  $Ti_2Ni$  alone (below 100  $cm^3/g$ ) could be reached at room temperature. Saturation of this composite with hydrogen (300  $cm^3/g$ ) could be reached at room temperature under a pressure of 6 MPa only. Hydrogenation of the  $TiFe + 57\% Ni$  composite was done in cycles, under a pressure of 4 MPa at a temperature of 450°C after prevacuumization. Hydrogenation of both  $LaNi_5 + 50\% Ni$  and  $LaNi_5 + 50\% Cu$  composites was done under a pressure of 2.5 MPa. Microstructural examination of phase analysis revealed diffusional interphase interaction in  $Ti_2Ni + 37\% Ni$ ,  $TiFe + 57\% Ni$ ,  $LaNi_5 + 50\% Cu$  during sintering and no fracture during



hydrogenation to saturation, no interphase interaction in  $\text{LaNi}_5$  + 50% Ni during sintering and complete fracture during hydrogenation of this composite. References 8: 4 Russian, 4 Western.

2415/12223

CSO: 1842/95

UDC 669.046:621.762:539.2

## CORROSION RESISTANCE OF SINTERED ALLOY STEELS

Moscow IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: CHERNAYA  
METALLURGIYA in Russian No 2, Feb 87 (Manuscript received 22 May  
86) pp 76-77

[Article by P. N. Ostriuk, I. I. Grigorchuk and M. M. Gasik,  
Dnepropetrovsk, Metallurgical Institute]

[Abstract] The sintered Cr-Ni-Mo powder steels, SP-Cr3Ni1Mo0.25 and SP-Cr3Ni2.5M, were tested for high-temperature oxidation in an air stream flowing at a velocity of 1.83 m/s. Powders of Fe, Cr, Ni and Mo, mixed in a 40ML mixer for 30 min and homogenized by annealing for 3.5 h, were compacted under a pressure of 810 MPa and then sintered at a temperature of 1393 K in a hydrogen atmosphere. Isothermal oxidation of steel specimens with 7-8% porosity at temperatures covering the 723-1323 K temperature range in 150 K steps was monitored for 1 h at each temperature by the thermogravimetric method. On the basis of measurements were plotted first the loss of mass per unit surface area as a function of time and then the temperature dependence of the oxidation rate. The latter yielded a low apparent oxidation activation energy for both steels during the initial 210 s period, 11.89 kJ/mole for SP-Cr3Ni1Mo0.25 steel and 10.70 kJ/mole for SP-Cr3Ni2.5M steel, indicating a high initial oxidation rate but also an increased inhibition of oxidation with rising temperature so that the law of oxidation kinetics becomes logarithmic. References 4: 1 Russian, 3 Western (all in Russian translation).

2415/12223

CSO: 1842/94

UDC 669.184:669.775

## DESULFURIZATION OF METAL DURING SMELTING OF EXTRA-LOW CARBON STEEL IN ACID CONVERTERS

Moscow IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA METALLURGIYA in Russian No 2, Feb 87 (manuscript received 8 Apr 86) pp 27-30

[Article by D. Ya. Povolotskiy, O. K. Tokovoy, G. P. Uryupin, V. A. Ryavkin, G. A. Yefimov and A. G. Lukovich, Chelyabinsk Polytechnical Institute]

[Abstract] Smelting of extra-low carbon steel with less than 0.03% C in Chelyabinsk Metallurgical Plant converters with 140 tons capacity was studied for the purpose of determining the distribution of sulfur between metal and slag toward the end of the process after the blow. measurements and correlation analysis of the readings have yielded a linear dependence of the sulfur distribution factor  $\gamma_s$  and the basicity  $B = |CaO|/|SiO_2|$  of the slag as the MgO content increases from 1-3% to 7-8%, namely  $\gamma_s = -2.37 + 2.06 B$  with a 0.91 correlation coefficient. At a constant basicity, moreover, the sulfur distribution factor was found not to depend on the acidity of the slag. This confirms the dual role of FeO in the slag, while its content remains low, namely compensation of the detrimental effect of  $Fe^{2+}$  cations by the favorable effect of  $O^{2-}$  anions. The statistical frequency distributions of sulfur content in technically pure iron produced by conventional smelting and by an experimental new method respectively indicate that the new method shifts the mode downward to 0.006-0.010% S with not more than 0.008% S in 67% of samples, as compared with less than 0.010% S in only 32% of samples produced by the conventional method. The gist of the new method for lowering the sulfur content in the metal is to add CaO (lime) and  $CaMg(CO_3)_2$  (dolomite) to the slag so as to increase its basicity and then to lengthen the blow time by 12-15% with a 12 min long pause for draining the slag. References 8: 6 Russian, 2 Western.

2415/12223  
CSO: 1842/94

UDC 620.172.24:620.251.2

LENGTHENING SERVICE LIFE OF EVAPORATORS MADE OF TUNGSTEN FOR  
VACUUM APPARATUS

Kiev FIZIKO-KHIMICHESKAYA MEKHANIKA MATERIALOV in Russian Vol 22,  
No 6, Nov-Dec 86 (manuscript received 1 Aug 84) p 96

[Article by V. N. Polyakov, V. P. Karshin, V. N. Geminov and  
L. K. Gordiyenko, NATI (State All-Union Tractor Scientific Research  
Institute) Scientific-Industrial Association), Moscow]

[Abstract] The service life of existing evaporators made of tungsten wire for aluminum coating of steel is limited to not more than 10-15 cycles of 15-25 s at a temperature of 1300°C under a vacuum of  $10^{-3}$  Pa, owing to the interaction of W and Al. A metallographic study of broken-down evaporators based on X-ray spectral microanalysis has revealed that liquid Al diffuses along the W grain boundaries down to several microns deep, evidently causing brittle intergranular cracking at a rate which increases with thermal cycling. A remedy was found in coating the evaporator with  $W_3B_4$  or WSi, by thermodiffusional impregnation in a powder bath in an argon atmosphere at a temperature of 1100-1200°C for 3-5 h. The evaporator life can thus be extended to 36 cycles with a  $W_3B_4$  coating and to 40 cycles with a WSi coating.

2415/12223  
CSO: 1842/76

**STATISTICAL EVALUATION OF STRUCTURAL CHARACTERISTICS AND  
HARDENING OBTAINED BY ROLLING SINTERED TUNGSTEN**

Kiev POROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87  
(manuscript received 27 Aug 85) pp 85-91

[Article by Ye. E. Zasimchuk, I. F. Zvorygin, B. G. Grafov,  
Ye. M. Rabinovich and G. P. Susanina, Metal Physics Institute,  
UkSSR Academy of Sciences]

[Abstract] Structural nonhomogeneity of hot-rolled tungsten strip and sheet made of sintered powder metal has been attributed to strain localization at grain boundaries and nonuniform volume distribution of impurities. For a further study of this problem, changes in the microhardness distribution and in the total area of metallographically discernible grain boundaries, depending on the percentage reduction by rolling, were evaluated by statistical methods on the basis of hardness measurements with a PMT-3 tester and X-ray structural analysis with a  $\text{CuK}_\alpha$ -radiation source. Specimens of sintered 99.95% pure tungsten were rolled in a protective atmosphere at an absolute temperature half-way below the melting point. Rolling of a wedge yielded a continuously and monotonically variable reduction of one specimen. Structural examination was done on 8 mm thick and  $10 \times 20 \text{ mm}^2$  large plates, in a plane parallel to the rolled surface but 5-10 mm underneath it as well as in a lateral plane and in an end plane. The results reveal an enlargement of microstructural elements upon 4-12% reduction and maximum hardening upon 24-26% reduction. References 8: all Russian.

2415/12223

CSO: 1842/78



UDC 546.57:542.942.7:621.775.7

METALLIC Ag POWDER PRODUCED BY REDUCTION OF Ag SALT WITH METOL

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 14 Oct 85) pp 5-8

[Article by A. A. Ryabukha, O. V. Koleshova, and V. P. Karlov,  
All-Union Scientific Research Institute of Reagents and  
Chemically Pure Materials for Electronic Technology]

[Abstract] Silver in powder form was produced experimentally by reduction of a soluble Ag salt with metol. High-purity industrial  $\text{AgNO}_3$  and grade-1 metol were used as working materials for this study, their concentrations in water being monitored by potentiometric titration with  $\text{NaCl}$  and  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (Mohr's salt) respectively while the molar ratio  $\text{C}_7\text{H}_9\text{ON}_2 \cdot \text{H}_2\text{SO}_4 : \text{AgNO}_3$  was varied from 0 to 1. The precipitate was washed first with 3% aqueous  $\text{NaNO}_2$  solution and then with 60-65 C hot water for removal of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  ions, an equimolar mixture having produced 99.5% powder and 5% excess metol. After drying at  $100 \pm 5^\circ\text{C}$ , the powder had a specific surface area of 0.19-0.21  $\text{m}^2/\text{g}$  and a bulk density of 2.4-2.9  $\text{g}/\text{cm}^3$ . Its grains were either polyhedral of the 0.5-20  $\mu\text{m}$  size fraction or oval of the 0.3-0.45  $\mu\text{m}$  size fraction. The powder contained only 98.7% Ag, having absorbed not only inorganic impurities but also organic ones removable by special solvents such as ethanol or acetone. Despite these impurities, the powder was found to be usable for electrical high-conductivity coatings. A paste made of this powder and an organic binder on a glass substrate had, after baking at  $700^\circ\text{C}$  in an electric furnace, an electrical resistivity of 0.11-0.12  $\Omega/\Omega\cdot\text{mm}$ . References 9: all Russian.

2415/12223  
CSO: 1842/95

## NEW GENERATIONS OF CERAMICS

Moscow VESTNIK AKADEMII NAUKA SSSR in Russian No 2, Feb 87 pp 98-111

[Article by Yu. D. Tretyakov, corresponding member of the USSR Academy of Sciences: "New Generations of Ceramics: Chemical and Technological Aspects"; text in slantlines printed *italic*]

[Text] Modern scientific-technical progress is indissolubly linked to the creation and introduction of new materials, among which ceramics play an increasingly important role. Although ceramics are a very ancient material in the history of human civilization, the "ceramic boom" noted several years ago is related not to traditional, but to fundamentally new types of ceramics which provide or promise to provide revolutionary changes in power engineering, microelectronics, computer and space technology, medicine, and transportation. New ceramic materials have opened new paths to the creation of high-temperature internal combustion engines and chemical current sources with high specific energy content and have made possible previously unheard-of metal cutting speeds.

Since ceramics now include any polycrystalline materials produced by sintering nonmetal powders, the spectrum of modern ceramic materials is very broad and exceptionally diverse in terms of material composition, structure, properties (functions), and applications. By composition, ceramic materials may be classified first of all as oxygen-containing and oxygen-free, among which one can single out carbides, nitrides, sulfides, fluorides, etc. In structure, ceramics may be amorphous, single-phase crystalline (spinel-perovskite-, garnet-like materials), as well as composite. Electrical, mechanical, optical, magnetic, and biological are among the primary properties (functions) of ceramic materials. The table shows the best shown types of ceramic materials with their special functions and applications.

The variety of ceramics' properties and functions makes it possible to use them to replace or supplement (thanks to ceramic coatings) traditional types of materials and particularly important metals such as tungsten, cobalt, and chrome. Moreover, new generations of ceramics are achieving record-breaking figures in terms of several indicators. Sialons, for example, surpass all known tool steels in resistance to thermal shock and wear and in cutting properties. New generations of ceramics make it possible to create fundamentally new structures such as thermal machines operating on the

## Applications of Different Types of Ceramic Materials

| Functions and types                        | Composition                                                                                                                                                  | Application                                                                                                                                                                        |
|--------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Electrical materials</b>                |                                                                                                                                                              |                                                                                                                                                                                    |
| Dielectrics                                | $\text{Al}_2\text{O}_3$ , $\text{BeO}$                                                                                                                       | Integrated circuit substrates                                                                                                                                                      |
| Ferroelectrics                             | $\text{BaTiO}_3$ , $\text{SrTiO}_3$                                                                                                                          | Condensers                                                                                                                                                                         |
| Piezoelectrics                             | $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$                                                                                                                  | Vibrators, filters, generators, resonators, converters                                                                                                                             |
| Semiconductors                             | $\text{ZnO}$ , $\text{ZnO}+\text{Bi}_2\text{O}_3$<br>Transition metal oxides                                                                                 | Varistors<br>Thermistors with negative and positive resistance factors                                                                                                             |
|                                            | $\text{La}_{1-x}\text{CaCrO}_3$ , $\text{SiC}$                                                                                                               | Electric furnace heaters                                                                                                                                                           |
|                                            | $\text{CdS}$                                                                                                                                                 | Solar battery photoconverters                                                                                                                                                      |
| Electron-ion semiconductors                | Oxides of bronze, chalcogenide inclusion compounds                                                                                                           | Electrode materials                                                                                                                                                                |
| Ion conductors                             | $\text{ZrO}_2(\text{Y}_2\text{O}_3)$<br><br>$\beta\text{-Al}_2\text{O}_3$                                                                                    | High-temperature electrolyzers, oxygen detector, high-temperature heaters<br>Solions, storage cells with high specific energy content                                              |
| <b>Magnetic materials</b>                  |                                                                                                                                                              |                                                                                                                                                                                    |
| Magnetically soft ferrites                 | $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$                                                                                                            | Secondary transformers for color televisions, magnetic heads for video recorders                                                                                                   |
| Ferrites with rectangular hysteresis loops | $\text{Li}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$                                                                                                            | Computer memory elements                                                                                                                                                           |
| Magnetically hard ferrites                 | Hexaferrites of barium, strontium, lead                                                                                                                      | Permanent magnets                                                                                                                                                                  |
| <b>Structural materials</b>                |                                                                                                                                                              |                                                                                                                                                                                    |
| Superhard                                  | $\text{Al}_2\text{O}_3$ , $\text{TiC}$ , $\text{TiN}$                                                                                                        | High-speed cutting tools                                                                                                                                                           |
| Wear-resistant                             | $\text{Al}_2\text{O}_3$ , $\text{ZrO}_2$ , $\text{TiC}$ , $\text{TiN}$ , $\text{BN}$ , $\text{NbC}$                                                          | Ceramic bearings, draw plates, grinding equipment                                                                                                                                  |
| Heat-stable                                | $\text{SiC}$ , $\text{Si}_3\text{N}_4$ , sialons                                                                                                             | Ceramic motors, turbine blades, heat exchangers                                                                                                                                    |
| <b>Optical materials</b>                   |                                                                                                                                                              |                                                                                                                                                                                    |
| Transparent ceramics                       | $\text{Al}_2\text{O}_3$<br>$\text{MgO}$ , mullite<br><br>$\text{Y}_2\text{O}_3\text{-ThO}_2$<br>$\text{Pb}_{1-x}\text{La}_x(\text{Zr}, \text{Ti})\text{O}_3$ | High-pressure sodium-vapor lamps<br>Optical elements for the infrared band<br>Lasers<br>Optoelectronic memory elements, video systems for recording, storing, and reproducing data |

# Applications of Different Types of Ceramic Materials — continued

| Functions and types                            | Composition                                            | Application                                                                         |
|------------------------------------------------|--------------------------------------------------------|-------------------------------------------------------------------------------------|
| <b>Heat engineering materials</b>              |                                                        |                                                                                     |
| Heat conductive ceramics                       | $\text{Al}_2\text{O}_3$                                | Recuperators, heat exchangers                                                       |
| Heat insulation ceramics                       | $\text{ZrO}_2(\text{CaO})$                             | Heat insulation coatings                                                            |
| Heat-stable ceramics                           | BN, $\text{ThO}_2$ , $\text{ZrB}_2$ , $\text{TiB}_2$   | Metallurgical equipment                                                             |
| <b>Materials with chemical properties</b>      |                                                        |                                                                                     |
| Porous ceramic agglomerates                    | $\text{Al}_2\text{O}_3$ , cordierite                   | Catalyst carriers                                                                   |
| " "                                            | $\text{SnO}_2$ , $\text{ZnO}$ , transient metal oxides | Chemical detectors for water vapor, hydrogen, oxygen, hydrocarbons, carbon monoxide |
| <b>Materials for nuclear power engineering</b> |                                                        |                                                                                     |
| "Fuel" ceramics                                | $\text{UO}_2$ , $\text{ThO}_2$ , UC                    | Reactor fuel elements                                                               |
| Radiation-proof ceramics                       | $\text{Al}_2\text{O}_3$ , SiC, $\text{B}_4\text{C}$    | Reactor insulation                                                                  |
| <b>Materials for medicine</b>                  |                                                        |                                                                                     |
| Ceramics with bio-logical compatibility        | Tricalcium phosphate $\text{Al}_2\text{O}_3$           | Dental repair and orthopedic surgery                                                |
| Porous ceramics                                | $\text{Al}_2\text{O}_3$                                | Removal of antibiotics from an organism                                             |
| Magnetoactive ceramics                         | Ferrites                                               | Diagnostics                                                                         |

principle of concentrated electrochemical elements, or gas-turbine engines which, thanks to an increase in working temperature to  $1,500^\circ\text{C}$ , become highly economical, capable of running on many fuels, and ecologically preferable. (Footnote 1) (Kulik, O. P., Denisenko, E. G., Krot, O. I., "High-Temperature Structural Ceramics. Derivation and Properties." Preprint No. 2, Kiev: IPN AN USSR [UkSSR Academy of Sciences Institute of Materials Science Problems, 1985.]

The ceramic boom is characterized particularly by the fact that major concerns and companies in the West, including giants such as Standard Oil, Union Carbide, Dow Chemical, etc. are involved in production of ceramic materials. (Footnote 2) (Sanders, H. Y., "High-Tech Ceramics," Chem. and



Especially favorable technical-economic, financial, and sociopolitical conditions for the development and widespread use of new types of ceramics have been developed in Japan, where production of precision ceramics should triple in the next 5 years. Japanese companies have assumed a dominant position in the production of ceramic materials for the electronic, radio, and related branches of industry. Meanwhile, the USA dominates the field of structural ceramics, which are intended primarily for metal processing. To judge by predictions, this situation will continue until the beginning of the next century.

The prospects for ceramics as a material of the future depend on many factors, the most significant of which are:

1. The basic types of ceramics are polyfunctional, so that a huge number of materials for different purposes can be created on the basis of a comparatively limited number of individual chemical compounds. These include primarily aluminum oxide, zirconium dioxide, and silicon carbide and nitride. The polyfunctional nature of ceramics can be illustrated by materials based on  $Al_2O_3$  (cf. table).
2. Raw material for ceramics production is relatively accessible, including material for producing oxygen-free ceramics such as silicon carbides and nitrides.
3. Compared with metals, ceramic materials possess higher corrosion and radiation resistance.
4. Ceramic materials possess greater biological compatibility than do metals and polymers, which permits them to be extensively used both in medicine and as structural materials in biotechnology and genetic engineering.
5. Ceramics, more so than metals and polymers, offer the opportunity to create new materials with preassigned mechanical, magnetic, electrical, and other properties and characteristics. The required results can be achieved by altering chemical composition (almost all the elements on the periodic table can be added to the composition of ceramics by different types of bonds) or phase composition (there are ceramics based on individual compounds, solid solutions, and composites). But the most important factor here is the structural diversity typical of all levels of structure — both for the crystalline structure and substructure inherent in any solid bodies, and for the ceramic structure specific to ceramics, i.e. a crystallite structural organization of identical or different composition within a polycrystal body. Any, even the smallest, ceramic product consists of a large number of crystallites, whose size, shape, and relative arrangement greatly determine structure-dependent properties. Hence, there is definite promise of further microminiaturization of instruments using ceramic elements.



It is obvious that an attempt can be made to use any of these possibilities to achieve the assigned properties in a ceramic material. It is not always clear, however, how to do this in the most efficient manner. Success was often achieved in the past (as it sometimes is now) thanks to specialists' experience, skill, and empirical knowledge, gained through long work with ceramic material. Abroad, especially in Japan, most companies have highly skilled workers whose experience borders on artistry.

It is important to mention that all stages in the existence of ceramic materials, beginning from production and ending in destruction after long use, are intimately related to chemistry. The chemistry of ceramic materials (ceramochemistry) is rapidly developing, but the variety of these materials is now so diverse and will become so much more so in the near future that advances cannot be made without relying on principles which derive from the commonality of the physico-chemical properties of different processes and materials.

A systems approach is needed to solve two key problems -- creating ceramic materials with the required properties and functions, and developing an efficient technology for producing these materials with replicable characteristics in the quantity required. In the first case, we must rely on a certain system of chemical and physico-chemical principles which are applicable in the development of not only ceramic, but also of other new solid-phase materials. (Footnote 3) (Tretyakov, Yu. D., "Principles of the Creation of New Solid-Phase Materials," *Izv. AN SSSR, Neorgan. materialy* [Proceedings of the USSR Academy of Sciences, Inorganic Materials], 1965, vol. 21, No. 5, pp. 693-701; Tretyakov, Yu. D., "Chemical Principles of the Design of Solid-Phase Materials," *Izv. SO AN SSSR, ser. khim. nauk* [Proceedings of the Siberian Branch of the USSR Academy of Sciences, Chemical Sciences Series], 1982, No. 6, pp. 16-21.) These principles also determine the practical possibilities for acting on the material to be created. In the second case, we must use a system of factors which as a totality ensures minimum energy, labor, and material expenditures, as well as expenditures related to nature preservation.

These chemical and physico-chemical principles will be considered below with several examples of the creation of new generations of ceramics.

It follows from the principle of /periodicity/ that the set of chemical elements ordered according to periodic law is broken down into subsets, i.e. rather closed sets of elements whose compounds, just like the materials on which they are based, exhibit similar properties. One might recall that almost all ceramic electrolytes with high cationic conductivity, for example, are compounds of the elements in the first group (lithium, sodium, potassium, rubidium, cesium, copper, silver), while electrolytes with high anionic conductivity constitute a compact field including compounds of fluorine, chlorine, bromine, iodine, oxygen, and sulfur.

Chemical elements on which modern structural materials are based also form a compact group in the periodic system of elements. These elements include

boron, carbon, nitrogen, oxygen, aluminum, silicon, titanium, germanium, and zirconium. The most widely used are binary compounds formed in some way by two of these elements (primarily  $\text{Al}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ ,  $\text{ZrO}_2$ ). Recently, however, there has been a trend developing toward combining binary compounds in the form of solid solutions or composites. The most obvious example is the creation of sialon — a solid solution of a heterovalent substitution of  $\text{Si}_{6-x}\text{Al}_2\text{N}_3-x\text{O}_x$ , thermodynamically stable in the Si-Al-O-N system at  $0 < x < 5$ .

The combination of these binary compounds affords the opportunity to create materials which possess a unique combination of properties: low density (almost 2.5 times less than that of iron, 6 times less than that of molybdenum and tungsten), a low coefficient of thermal expansion (4-5 times lower than that of iron and 10 times lower than that of aluminum), low thermal conductivity (3 times lower than that of iron), high refractory qualities, hardness, wear- and corrosion resistance, and the ability to maintain near-constant strength at temperatures from room to  $1400^\circ\text{C}$  (i.e.  $200-400^\circ\text{C}$  higher than the working temperatures of superalloys).

All these advantages have attracted attention to silicon and boron carbides, silicon and aluminum nitrides, and aluminum and zirconium oxides as structural materials for various purposes. These are basically materials for gas-turbine and diesel engines, in which certain parts, including moving and nonmoving blades, combustion chambers, heat exchangers, rotors, compressors, and recuperators, may be made from ceramics. These engines will permit a fuel savings up to 30 percent. The increase in temperature in the combustion chamber to  $1300^\circ$  means that the most varied types of fuel can be used as the combustible. This high temperature in the combustion chamber considerably boosts engine efficiency under partial loads, and, because of more complete fuel combustion in cylinders, the level of exhaust gas toxicity declines.

Intense research on carbides, nitrides, borides, and oxides as the basis for creating a new generation of materials is being done in the UkSSR Academy of Sciences' Institute for Problems of Materials Technology, the USSR Academy of Sciences' Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, the Institute of Chemistry of the USSR Academy of Sciences' Ural Scientific Center, and other academic and branch institutes.

/Physico-chemical analysis/ plays an exceptionally important role in the creation of the new generation of ceramic materials. Appropriate measurements makes it possible to establish the relationship between the composition and properties of equiponderant systems and to plot their constitution diagrams.

A large amount of material on composition-property diagrams and on equiponderant constitution diagrams for ceramic-forming systems has been compiled from many years of research conducted at the USSR Academy of Sciences' Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, the USSR Academy of Sciences' Institute for Silicate Chemistry imeni I. V. Grebenshchikov (ISC), the UkSSR Academy of Sciences' Institute

of Materials Science Problems, and many others. The demand for data on multicomponent (primarily oxide) systems has recently grown tremendously. At the same time there are still many blank spots, even in certain binary systems such as  $\text{ZrO}_2\text{-CaO}$  and  $\text{Na}_2\text{O-Al}_2\text{O}_3$ , important for creating MGD [magnetohydrodynamic] generators and electrochemical current sources. Although the technology for physico-chemical analysis has recently been enriched by fundamentally new systems for heating and cooling and for thermal and structural analysis, the very nature of these subjects creates barriers which are difficult to overcome (e.g. in studying equilibria with phases in whose structure anion and cation sublattices possess drastically different component mobility).

Especially important for creating new generations of ceramics are systems involving oxides of rare earth elements, as well as dioxides of silicon, titanium, germanium, zirconium (the Silicate Chemistry Institute plays an important role here), phosphate systems (the scientific school of Academician I. V. Tananayev at the General and Inorganic Chemistry Institute, ferrite-forming systems (Metallurgy Institute of the USSR Academy of Sciences' Ural Science Center), oxygen-free systems with the formation of heat-resistant phases (Materials Science Problems Institute), and vanadate (USSR Academy of Sciences' Ural Science Center Chemistry Institute), tungstenate, niobate, and tantalate systems.

The fundamental works of A. S. Berezhnoy, Academician of the UkSSR Academy of Sciences, are making a substantial contribution to the study of multicomponent oxide systems. The development of physico-chemical analysis of systems involving metastable phases is just as, and perhaps more, important than knowledge of equilibrium constitution diagrams to the creation of new ceramic materials (Footnote 4) (Shults, M. M., Borisova, N. V., Kozhina, Ye. L., "Thermodynamics of Heat-Resistant Oxide Systems in the Light of Criteria of Equilibrium Stability," *Khimiya silikatov i oksidov* [Chemistry of Silicates and Oxides]. Leningrad, Izdatelstvo "Nauka," 1982, pp. 3-19.)

Principles of /structural disorder/ and /unstable composition/ in solid-phase compounds have turned out to be exceptionally fruitful not only in the chemistry of semiconductors and especially pure substances, developed respectively by the schools of Academician A. V. Novoselovay (Moscow State University) and Academician G. G. Devyatyye (Chemistry Institute of the USSR Academy of Sciences), but also in the development of new types of magnetic and piezoelectric ceramics, ceramic electrolytes, and electron-ion conductors based on lithium-vanadium bronzes. The idea of ferrites as compounds with variable composition has enabled us to understand and then eliminate the causes of many failures related to the irreproducibility of ferrite parameters, both at the production stage and during use. (Footnote 5) (Tretyakov, Yu. D., *Khimiya nestekhiometricheskikh oksidov* [The Chemistry of Nonstoichiometric Oxides]. Moscow, Izdatelstvo MGU [Moscow State University], 1974.)

Closely related to the principle of disorder and instability of solid-phase



compound composition, the principle of /equivalence of the sources of disorder/ when free energy is minimized (Weill's principle) is also effective in ceramics materials technology. The principle states that a solid-phase, including ceramic, material formed in any way spontaneously acquires the type of defects which ensure the maximum increase in entropy for the least energy expenditures.

Use of Weill's principle has made it possible to obtain transparent ceramics based on yttrium oxide by alloying it with zirconium or thorium dioxide and to understand such seemingly paradoxical phenomena as the increase in the rate of solid phase reaction upon exposure to a chemically inert material, the reduction in the intensity of processes involving highly active oxides when temperature increases, and much more.

The principles of /chemical, structural, and phase complication of composition/ are quite extensively used in ceramic materials technology and, in addition, are often considered as a universal means of achieving the goal. The diversity of the consequences of alloying is not always considered. These consequences greatly depend on the nature of the chemical bond in the matrix and the physico-chemical nature and method of distribution of additives. In addition, in forming a solid solution of isovalent or heterovalent substitution, additives change the concentration of point and extended defects, affecting structure-sensitive characteristics — magnetic, electrical, and optical. Concentrated on dislocations, impurities reduce their mobility and slow the speed of processes with a dislocation mechanism; but undissolved, they hinder the material's recrystallization while altering the density and strength of the ceramics, its deformation resistances, and other characteristics.

Structural complication results from the fact that additives usually have limited solubility and, long before the limit is achieved, cause a restructuring similar to changes in nonstoichiometric phases. Structural complication of a solid phase material usually means a loss of elements of symmetry, which in accordance with Curie's principle is seen in a change in the symmetry of the material's properties. If structural complication in a crystal results in polar axes, it manifests piezoelectric properties; if it has a single polar axis, then the crystal is simultaneously pyroelectric.

The principle of phase complication has served as the basis for creating new types of composites, particularly metal-hardened ceramics. These ceramics, based on  $\text{Al}_2\text{O}_3$  are twice as strong as ordinary. They are also heat-resistant and impermeable by liquids and gases in a high-temperature oxidizing medium. Material containing 1 percent metal phase (chrome, platinum) has a fracture resistance of  $K_{Ic} > 6 \text{ MNm}^{-3/2}$ , which is much higher than that in ordinary aluminum oxide ceramics. Ceramics containing uniformly distributed disperse metal particles in an oxide material possess special heat-stability. The optical characteristics of metals usually used as selective solar cell absorbers (high absorbability in the solar spectrum and low "blackness" in the infrared band, where the heated surface is irradiated), deteriorate considerably at  $250^\circ\text{C}$ , while ceramics reinforced by

the same metal particles function up to 1,000°C.

For SiC and Si<sub>3</sub>N<sub>4</sub> compounds with a strong covalent bond, phase complication techniques are used to intensify ceramic powder fritting processes. The most effective are oxides of rare earth elements which form liquid silicates with an SiO<sub>2</sub> inclusion, which is always present in raw silicon carbide or nitride, at a high temperature. Fritting becomes reactive and liquid-phase and results in high-quality structural ceramics for turbine engine rotors and stators. We must say that, because composite properties are highly sensitive to the size, shape, and spatial distribution of filler particles, chemical methods such as spinel decay, eutectoid crystallization, or cryochemical technology techniques must be used to produce them.

A key principle in ceramic materials technology is the use of production processes which ensure the required degree of product /uniformity/: chemical, granulometric, phase, and ceramic. Multicomponent and multiphase materials for microelectronics exhibit particular sensitivity to the degree of uniformity or nonuniformity. The more complex a material in the chemical or phase sense, the more difficult it is to ensure replicability of its properties.

Ferrite microcores — computer memory components — are difficult to see with the naked eye. Their diameters reach 0.2 mm, and 1 gram of ferrite powder can yield thousands of such cores. They function efficiently only in the presence of high chemical and ceramic uniformity. This was precisely the goal of the development of cryochemical methods for producing ceramic powders. These methods are based on a well balanced combination of heating and cooling; the latter is used to prevent uncontrollable changes in intermediate and finished products and purpose-specific regulation of their properties.

Cryochemical methods constitute a set of processes, primary among which is cryocrystallization, i.e. the freezing of salt solutions of ceramic-forming components to ensure hardening of both the solvent and the solutes and maintenance of the high chemical uniformity inherent to the initial solution in the solid phase. (Footnote 6) (Anastasyuk, N. V., et al., "Physico-Chemical Principles of Producing Solid Salt Solutions by Cryochemical Method," Izv. AN SSSR, Neorgan. materialy, 1974, vol. 10, No. 7, pp. 1307-1310.) Products derived in the form of cryogranules are dehydrated by sublimation drying or cryoextraction and are then subjected to heat treatment to obtain disperse ceramic powders. These powders are characterized by high chemical, granulometric, and phase uniformity in their basic components and inclusions, microplasticity, high reactive capacity and activity in solid phase processes, as well as easily regulated uniformity of the ceramic structure of the products of fritting.

One might ask, how uniform should a material be? The answer depends on the purpose and service functions of the ceramics: it must be as uniform as required to ensure the set of assigned properties and their replicability.



This assertion is not entirely trivial. The need for chemical uniformity is usually self-evident, but the tolerability of a certain degree of nonuniformity is not entirely obvious. From the standpoint of process efficiency and economy, it makes no sense to purify and homogenize substances if they are contaminated in later processes or if the existing nonuniformities are insignificant in the replicability of performance characteristics.

There are often cases when the required ceramics properties are attained with a totally specific, optimum chemical nonuniformity. This is seen with particular clarity in composites, whose record-breaking mechanical properties are achieved with the dimensions of chemically different matrix and filler particles optimum. The polycrystallinity and micrononuniformity of the structure of magnetic ceramics is a necessary condition to ensure a rectangular hysteresis loop. The structural nonuniformity of ion crystals causes their anomalous transfer properties until a super-ion state is achieved.

The /identical effect of various physico-chemical actions/ has long been used in ceramic materials technology. For example, the cubic modification of  $ZrO_2$ , which, in the absence of inclusions, forms from the tetragonal only at a temperature above  $2370^\circ C$ , is thermodynamically stable at  $1,400^\circ C$  and kinetically stable at an even lower temperature if it is alloyed with calcium oxide  $CaO$  (about 15 mole-percent). Moreover, a similar cubic  $ZrO_2$  stabilization effect is achieved if  $Y_2O_3$ ,  $MgO$ , or certain oxides of rare earth elements are used instead of  $CaO$ . The transition of the tetragonal modification of  $ZrO_2$  to the cubic may take place even at room temperature as a result of neutron irradiation.

The use of high temperatures in solid phase interaction is successfully replaced by mechanochemical treatment of reaction mixtures. Mechanochemical action favorably alters many ceramic powder properties. For example, ferrite plasticity increases considerably, so that there is no need to introduce organic plasticizers. The prospects of introducing mechanochemical processes into the technology for new types of ceramics are related in our country to the completion of the program headed by V. V. Boldyrev, corresponding member of the USSR Academy of Sciences (Institute of Solid State Chemistry and Mineral Processing of the USSR Academy of Sciences).

The use of nontraditional physico-chemical actions, including laser irradiation, ion implantation, blast waves, high-frequency electrical fields, electrophoresis, vibration, plasmochemical and cryochemical processes, creates a wide range of opportunities in the attempt to obtain the required effect from altering ceramic properties.

The significance of the /nonequivalence of volumetric and surface properties/ in ceramic materials science can now be recognized in the light of the fundamental works of I. V. Tananayev, who specifically showed the need to establish a correlation among composition, structure, dispersion,

and properties. (Footnote 7) (Tananayev, I. V., "Prospects for Development of Research in the Area of Certain Inorganic Materials," *Izv. AN SSSR, Neorgan. materialy*, 1971, vol. 7, No. 2, pp. 361-366.) We must consider that a material's intercrystalline surface, in addition to its geometric surface, is exceptionally important in the formation of ceramic properties -- its length and composition, which are in turn determined by the size and shape of crystallites, as well as by the size, shape, and distribution of pores and foreign inclusions.

The formation of properties begins with ceramic powders, whose disperse state is ensured by the use of various physico-chemical processes. These include: mechanochemical dispersion, co-precipitation, thermal decomposition of salts, cryomechanical, plasmochemical, and "sol-gel processes." The particular attractiveness of the latter stems from the high quality of products: their purity, chemical uniformity and particle size, easily controlled from 0.003 to 0.1 microns."

The essence of the "sol-gel process" consists in the fact that ceramic-forming metals reacting with alcohol become alcoholates, which dissolve in alcohol and further hydrolyze under conditions leading to the formation of a sol, and then a gel. Quite recently it was shown that, if the amorphous product formed during hydration is exposed to ultrasound and then separated from the liquid by centrifuging, the result is a ceramic powder containing spherical particles less than a micron in size which, after molding and fritting, yield a ceramic with a density near x-ray and with crystallites measuring about 0.5 microns. Even this, however, is insufficient to demonstrate the effect of microplasticity, which reduces material brittleness. The most promising methods in this sense are those based on production of ceramic powders not from the liquid, but from the vapor phase formed because of laser or plasmochemical action.

For example, with a CO<sub>2</sub> laser as a heat source, gaseous reagents such as SiH<sub>4</sub>, NH<sub>3</sub>, and C<sub>2</sub>H<sub>2</sub> were used to produce ultra-dispersed silicon carbides and nitrides consisting of spherical particles of about the same size (from 0.012 to 0.1 micron, which do not tend to aggregate. There are reasons to anticipate advances in the laser synthesis of other ceramic products, including aluminum and titanium oxides, boron and tungsten carbides, and aluminum nitride.

Considering that the surface and near-surface layers of a material most often do the "work" under service conditions, the attempt to affect a material's property through its surface is natural. Heat-resistant ceramic coatings on rocket engine parts made of superalloys are an example. It has been discovered that if a ZrO<sub>2</sub> coating stabilized by the oxide Y<sub>2</sub>O<sub>3</sub> produced by plasma spray is laser-processed, a layer of microcracks which substantially improve the parts' erosion resistance and prevent the catastrophic consequences of mechanical overloads forms in this coating. Modern research methods, including Auger spectroscopy, emission spectroscopy for chemical analysis, etc. make it possible to understand the nature of the special status of a ceramic material's surface as compared with its status

in a volume.

/Metastable diversity/ may play both a positive and a negative role, since the diversity of materials formed from the same chemical composition is desirable when it is completely controlled, but extremely undesirable when, for subjective or objective reasons, this control is impossible. This circumstance is closely linked to the solution of a very important technological problem: how to produce ceramic material with a specific level of properties and how to ensure replicability of these properties when this material is produced on the necessary scale.

For example, in the electronics industry, multi-ton output of magnetic ceramics is most often organized using ferrite powders as raw material. The fritting process is basic in this situation, and as a result the mass of powder-forming particles of green sand molding become a mass of crystallites bound more or less firmly in the product of fritting. It is obvious that the initial particles, even with set chemical and phase composition, may be produced by various methods differing from one another in the nature and dispersion of substructure defects, particle size and shape, their mutual arrangement, etc.

The results of the conversion operation (fritting in this case) are also ambiguous because of the limitations of the transfer of mass, energy, and impulse resulting from the diversity of effects on individual parts of the system (macrokinetic limitations). A certain indeterminateness in the structural state of the finished product is inevitable and results in the indeterminateness (spread) of structure-sensitive ceramic properties.

Naturally, the indeterminateness of the status of the end product, just as the spread of its structure-sensitive properties, may be diminished by strictly controlling the molding of the ceramic directly from a uniform medium. This medium might be the liquid or vapor phase, whose uniformity is much simpler to ensure than that of the solid phase.

Obviously, the very conversion process in this case also must be clear-cut. This can be ensured by dispersing the solution and subjecting its microvolumes to identical forces. This action, however, may cause certain elementary processes to combine: when solutions are atomized, there is a simultaneous evaporation of moisture, dispersion, thermal decomposition, and recrystallization. During combining, these elementary processes interact so strongly that the conversion process is extremely sensitive to variations in the parameters at which it is carried out (liquid feed rate, temperature, etc.), and the goal — to produce a material with replicable properties — is not attained.

A much more effective method is one which makes it possible to separate the operations of quantification and the physical and chemical processing of solutions. It was precisely this objective which was accomplished in the cryogenic method of producing ceramic materials discussed above.



Note that any ceramic product "senses" from what and how it was produced. That is, the effect of topochemical memory is manifest to a certain degree. Naturally, the huge number of methods for turning raw material into a product is reflected in a huge set of possible end product states. But even if it were possible to carry out all conversions in a strictly unequivocal way, the properties of the finished product would still depend on the properties of the raw material.

Indeterminateness may be compensated, although not always, by specific processing techniques. For example, if the initial ceramic powder is inert in fritting processes, the situation may be remedied by mechanochemical activation. If the raw material is in contrast excessively active, then a highly disperse, but inert filler, not capable of being dissolved in the matrix, should be introduced to prevent recrystallization processes. The topochemical memory of the raw material may be "erased" by other methods as well, including alloying of components which cause microliquifaction of the matrix or stabilization of a certain redox state in its forming ions. (Footnote 8) (Tretyakov, Yu. D., Tverdogaznyye reaktsii [Solid Phase Reactions]. Moscow, Izdatelstvo "Khimiya," 1978.)

At the same time the positive effect of topological memory can and must be used to create new ceramic materials with specific functions. The first steps in this direction have already been taken: the formation of an optimum ceramic structure in ferrites by using raw products obtained with the maximum possible system deviation from equilibrium.

This set of principles constitutes a system which defines chemical ways to solve any problems in ceramic materials technology.

Use of the system of physico-chemical principles has proven effective in the creation of new types of magnetic ceramics, ceramic electrolytes, and electron-ion conductors, piezoceramics and flexible piezocomposites based on them. Naturally, all these principles are related, and it is also obvious that this list is far from complete. Among those absent are, specifically, principles which define the behavior of open systems which exchange mass and energy with the environment and are described by thermodynamic disequilibrium functions (synergism).

Several basic and applied scientific and organizational problems must be solved on the way to creation of a new generation of ceramic materials. In the author's opinion, the following are the most urgent:

- development of ceramochemistry, especially physico-chemical principles for the creation, use, and recovery of ceramic materials;
- development of physico-chemical and technological techniques to overcome the defects of traditional structural ceramics, especially brittleness and inability to withstand thermal shocks;
- creation of effective physico-chemical processes for joining ceramic items

to one another;

- organization of the production of high-quality ceramic raw material with replicable properties and optimum rheological characteristics, including particle size and shape, chemical and granulometric uniformity, and activity in fritting processes;
- creation of specialized process equipment, including modules for flexible ceramics production;
- development of effective methods for post-operational control of ceramic processes and nondestructive testing of raw materials and intermediate and final products;
- training of specialists in solid state chemistry for creation of fundamentally new types of ceramics and radical improvement of technology;
- efficient coordination of academic science and science in institutions of higher learning and branches, as well as the efforts of specialists in chemistry, physics, mechanics, engineering, etc., related to obtaining and using ceramic materials;
- organization of international cooperation, primarily involving CEMA member countries through joint scientific technical projects and regular international meetings;
- creation of original and translation of the best foreign monographs and textbooks devoted to the chemistry and technology of the new generations of ceramic materials.

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# OXIDATION RESISTANCE AND MECHANICAL STRENGTH OF HOT-PRESSED $\text{Si}_3\text{N}_4$ CERAMICS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 28 Feb 86) pp 75-79

[Article by Yu. G. Gogotsi, I. I. Osipova, S. I. Chugunova and V. Zh. Shemet, Institute of Materials Science Problems, UkSSR Academy of Sciences, and Kiev Polytechnical Institute]

[Abstract] Oxidation of hot-pressed  $\text{Si}_3\text{N}_4 + 10\% \text{BN} + 5\% \text{MgO}$  ceramic in air at temperatures up to  $1500^\circ\text{C}$  was measured, BN having been added for improvement of the heat resistance and the dielectric properties. The material was produced in graphite dies at a temperature of  $1750 \pm 50^\circ\text{C}$ . Subsequent phase analysis in a DRON-2.0 X-ray diffractometer with a  $\text{CuK}_\alpha$ -radiation source revealed an amorphous phase in addition to  $\alpha\text{-Si}_3\text{N}_4$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiN}_2$ , and BN. Bars of this material 15 mm long and  $4 \times 4 \text{ mm}^2$  in cross-section were oxidized both isothermally and during heating at a rate of  $150^\circ\text{C}/\text{min}$ , measurements being made with an OD-103 derivatograph. Bars of the material 25 mm long and  $2.5 \times 4 \text{ mm}$  in cross-section were tested mechanically for strength in flexure by the 3-point method at a deformation rate of  $1 \text{ mm}/\text{min}$  in a 1246 machine with special Mo support under a vacuum of  $0.013 \text{ Pa}$  and at temperatures up to  $1200^\circ\text{C}$ . Detectable oxidation was found to be activated at temperatures close to  $1000^\circ\text{C}$ , although  $\text{Si}_3\text{N}_4$  had begun to oxidize at  $800^\circ\text{C}$  and  $\text{B}_2\text{O}_3$  had evaporated at  $900^\circ\text{C}$  with only a white film forming on the surface. Oxidation at  $1200\text{--}1500^\circ\text{C}$  was found to produce  $\alpha\text{-Si}_3\text{N}_4$ ,  $\text{Mg}_2\text{SiO}_4$  (forsterite),  $\text{MgSiO}_3$  (enstatite), and amorphous borosilicate glass. The mechanical tests revealed a temperature dependence of the strength, the latter peaking within the  $600\text{--}800^\circ\text{C}$  range, dropping to normal level at  $1000^\circ\text{C}$ , and dropping completely at  $1200^\circ\text{C}$ . These data are correlate with data on the apparent oxidation activation energy. References 17: 8 Russian, 9 Western (1 in Russian translation).

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## VITREOUS METALS

Moscow PRIRODA in Russian No 2, Feb 87 pp 80-88

[Article by A. Ya. Belenkiy: "Vitreous Metals"]

[Text] When we speak of a "crystal," we usually picture glittering druses of mineral crystal or the shimmering facets of a diamond, bodies which physics classifies as dielectrics. However, dielectrics, especially silicon oxide and silica, have been familiar to people for thousands of years in a vitreous, amorphous state. In contrast, opaque, shapeless metals are hardly associated with the image of geometrical regularity of a structure, and significant efforts were required of researchers to demonstrate their microcrystalline atomic structure. When the crystallinity of metals no longer raised anyone's doubts, vitreous metals were discovered.

## How We Learned to Obtain Metals in an Amorphous State

In 1959 two young staff members at California Institute of Technology (Pasadena, California) working under P. Duwez tried to use rapid hardening of a metal melt to obtain metal alloys as concentrated as possible in a solid state. Working with the Pd-Si system, they unexpectedly discovered that a droplet of a melt which has not crystallized vitrifies.<sup>1</sup> The high-speed hardening method they used (now called the "hammer and anvil" method) consisted in flattening droplets of the melt on the flat surface of a material with high thermal conductivity. Then a similar setup for high-speed hardening was created by I. S. Miroshnichenko and I. V. Salli, associates of Dnepropetrovsk State University.<sup>2</sup>

More modern methods of obtaining "metallic glasses" are based on the principle of "spinning a melt," in which a jet of molten metal under pressure is poured through a thin nozzle onto the surface of a rapidly rotating drum. The metal is cooled by 1,000°C in about one millisecond. This hardening speed is sufficient to suppress the crystallization process in many alloys, and there are now more than a hundred systems which change to an amorphous state.

There are several classes of these alloys. The most common are binary alloys of the following types: "transition metal-metalloid" (e.g. Pd-Si,

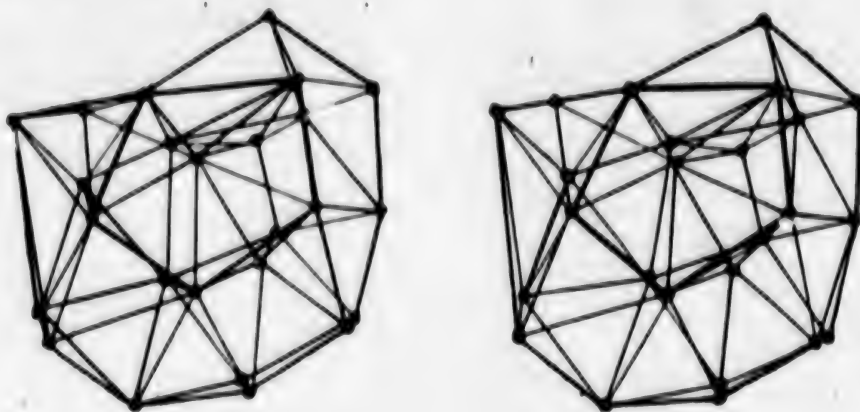
Fe-B, or Ni-P); "transition metal-transition metal" (Ni-Nb, Ni-Ta); "rare earth metal-transition metal" (Co-Gd, Fe-Gd); "nontransition metal-nontransition metal" (Mg-Zn, Ca-Al). Alloys with three or more ingredients have been developed for practical applications. The only common feature of easily amorphized systems is a rather strong chemical interaction among component atoms or, in other words, a rather large heat release during melting.

The metallic glass produced by spinning looks like a shiny, opaque strip several millimeters wide and 20-30 microns thick. Sometimes no special equipment is needed to produce an amorphous alloy. For example, the "amorphization record-holder," the alloy  $\text{Pd}_{78}\text{Cu}_6\text{Si}_{16}$ , is converted into glass if a droplet of a melt simply drops to the floor. This alloy has been successfully used to prepare amorphous pellets about 1 mm in diameter by casting droplets of the melt inside a hollow, helium-filled column 30 m high. Recently they have learned to produce massive amorphous specimens up to 1 cm in diameter by cooling the metallic melt in a stream of melted salt.

Diffraction methods can be used to reliably determine whether the resulting strip is in fact amorphous: during scattering of X-rays, neutrons, or electrons, one sees not the set of narrow lines typical for crystals, but rather several blurred intensity maxima indicating that the amorphous structure does not contain clear atomic planes that reflect the radiation. It is even simpler to check whether an alloy is amorphous by heating. At temperatures above 400-500°C (the flame of a match or gas burner), an amorphous alloy irreversibly crystallizes, which is usually accompanied by an abrupt change in its properties. For example, a strong, elastic amorphous strip becomes very brittle after crystallization. The irreversibility of crystallization confirms our understanding that the amorphous state is not truly stable — it is metastable.

Soon after the first metallic glasses were produced, it became clear that these new materials have quite valuable properties. Magnetic alloys based on transition metals (Fe, Co, Ni) are easily magnetized in the external field and easily change their magnetic state when the field changes. In combination with high electrical conductivity, which is 3-4 times greater than that of similar crystal alloys, these properties make amorphous alloys outstanding magnetically soft materials, which are widely used in electrical engineering: they are used to make cores for transformers, generators, and electric motors. Amorphous alloys are now the only mass-produced materials which make it possible to raise transformer efficiency above 99 percent, which means a savings of tens and even hundreds of billions of kilowatt hours of electricity per year on the scale of industrially developed countries.

The combination of electrical and magnetic properties permits highly efficient use of metallic glasses in magnetic amplifiers, filters, and other devices. Amorphous strip is used to produce magnetic screens to protect elements of electronic instruments, and its mechanical properties (unlike those of all other magnetic materials) allow these screens to simultaneously act as springs. They have already been used as such in designing tape recorder heads.



Stereoimage of a fragment of an amorphous structure obtained by computer modeling. To see the stereoimage, relax the eye muscles so that both images double and the inside pair of images merges (As per: A. Ya. Belenkiy, Doklady AN SSSR, 1985, vol. 281, pp. 1352-1355).

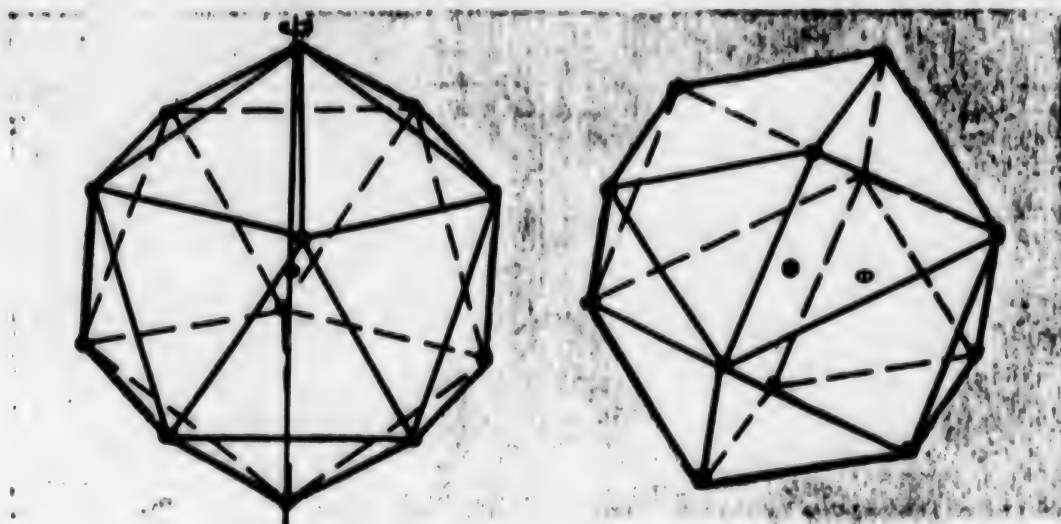
Vitreous metal alloys have served as the basis for creating strong, inexpensive, high-temperature solders. By special processing, amorphous magnetic materials can be used to make very efficient (efficiency above 90 percent) devices to convert magnetic energy into mechanical and vice versa. With good performance properties, metallic glasses are still "efficient to manufacture:" their production does not require large capital and energy expenditures, and they ensure high productivity and low-cost products. All these qualities have stimulated a great interest in the study and use of metallic glasses in the past 10-15 years, and thousands of tons are scheduled to be produced in the next few years in several industrially developed countries.

The great interest in the new class of materials among production engineers and metals scientists aroused a strong "fermentation of minds" also among representatives of the basic sciences. The fact is that the study of amorphous solid bodies (particularly metals) forced physicists to actually reconsider the traditional structure of solid state theory, which had been "resting on two elephants:" the ideas of the ideal crystal lattice and of defects related to its disturbance. Neither exists in an amorphous state. Therefore, the central problem of the physics of amorphous alloys was and is the most precise description of their atomic structure as the basis for calculating and predicting virtually all physical properties. We will now turn to the story of how "solid state" physicists are solving this problem.

#### Atomic Structure -- the Key to Predicting the Properties of New Materials

The beginning of theoretical works on studying the atomic structure of liquid and amorphous metals was research by J. Bernal in the beginning of





Icosahedron (left) and cubooctahedron. The colored line in the icosahedron denotes one of the fifth-order axes. When it turns  $2\pi/5=72^\circ$  around this axis, the figure superposes on itself.

the 60s. In these works he modeled an amorphous structure using several thousand metal balls arranged in a container. Subsequent efforts to model atomic structures on a computer showed that these structures are formed from various atomic groups which are noticeably distorted as compared with rectilinear geometric figures.

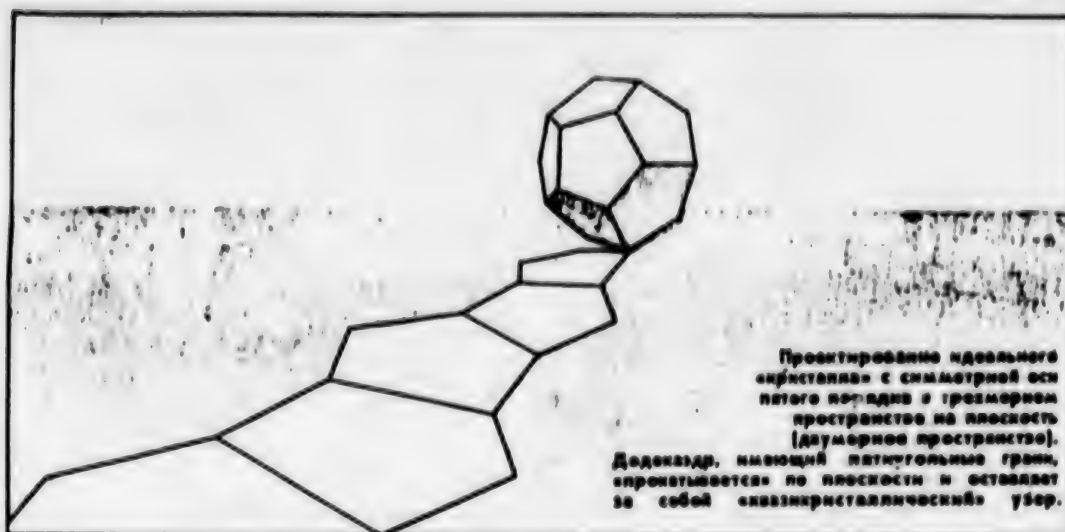
Experimental data were being collected while the modeling was being done. These data were used as the basis for the conclusion that there is a certain order in the arrangement of atoms at close distances in amorphous alloys. This means that atoms of one kind arranged next to atoms of another form groups resembling those which exist in corresponding crystal phases. For example, in "transition metal-metalloid" alloys, the most likely groupings are transition metal atoms forming a triangular prism around a metalloid atom. The metalloid atoms themselves have a tendency to separate from one another and are almost never found adjacent.

Although the very existence of a close order of atoms in amorphous alloys can now hardly be doubted, we still do not have enough experimental data to provide a clear picture of amorphous structure. It is possible that there is no such picture, but only more or less successful "reproductions" of it. It is appropriate to describe here one rather unusual model representation of amorphous structure intensively elaborated at present by theoreticians and which quite recently was unexpectedly confirmed by experiment.

#### Icosahedral Quasicrystals

It was noted as early as 1952 that, in terms of energy, it is more beneficial for a group of 13 atoms interacting by means of paired forces to form an icosahedron rather than a cubooctahedron, which is typical for the



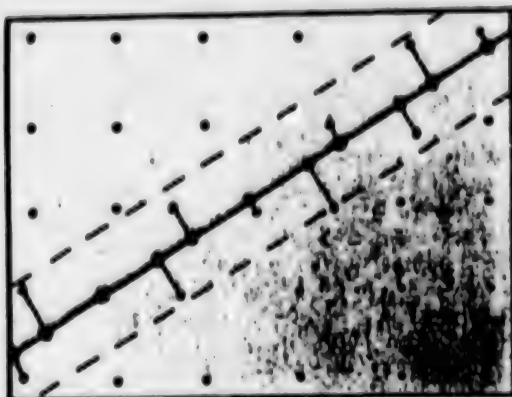


Projection of an ideal "crystal" with a fifth-order axis of symmetry in three-dimensional space on a plane (two-dimensional space). The dodecahedron with pentagonal faces is "rolled" over the plane and leaves a "quasicrystalline" pattern behind.

arrangement of adjacent atoms in a face-centered cubic lattice. An icosahedron, however, has a fifth-order axis of symmetry and cannot be the elementary cell of any crystal, since this symmetry is incompatible with the periodic arrangement of atoms. In other words, rectilinear icosahedra cannot fill an arbitrarily large space without defects and distortions, just as it is impossible for a plane to be "paved" by rectilinear pentagons.

The idea that adjacent atoms in certain amorphous alloys are configured into an icosahedron has been actively promoted in recent years by authors who have hypothesized that an amorphous structure is a certain "projection" of an ideal crystal with the symmetry of an icosahedron in four-dimensional space onto our everyday three-dimensional space.<sup>3</sup> The procedure for this design can be explained with the following two-dimensional example. Let us take a rectilinear polyhedron with pentagonal faces (called a dodecahedron), and smear its edges with paint. Then we roll it over a plane in different directions. As a result, a pattern of pentagons will be imprinted on the plane, interrupted somewhere by defects. The resulting structure, more precisely its three-dimensional analog formed by "rolling" a four-dimensional polyhedron (called a polytope) over a three-dimensional space, will on the whole be nonperiodic, but the icosahedral sequence may nevertheless continue over very great distances before it is disrupted by a defect.

Although this model of an amorphous structure looks at first glance rather artificial, it was first proven in computer models and then also by experiment. In 1984 it was announced that a structure with a fifth-order axis of symmetry had been discovered in the fast-hardening alloy

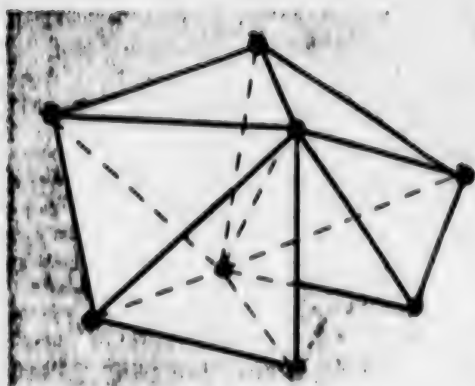


The plotting of a one-dimensional quasicrystal using the projection of a two-dimensional square lattice. Colored dots are projected images of the square lattice's nodes which lie in the band bounded by the broken line.

$\text{Al}_{86}\text{Mn}_{14}$ .<sup>4</sup> This result was like thunder in a clear sky. Subsequent experiments showed that the ordering in this "icosahedral" phase is preserved at distances on the order of one micron, i.e. very large on the atomic scale. Nor were theoreticians "napping:" they hypothesized several new descriptions of the structure and properties of an icosahedral crystal. One of these descriptions, the most elegant, was proposed by three students at Moscow Physical-Technical Institute, again using the idea of a projection of a multidimensional crystal.<sup>5</sup> According to their idea, atoms in the subject three-dimensional quasicrystal belong to a thin (with a thickness on the order of the distance between atoms,  $10^{-8}$  cm) "slice" of an ideal cubic lattice in six-dimensional space (!). It turns out that the slope of the "plane" of the slice can be matched to the edges of the six-dimensional cube, so that within this "plane" (which is nothing more than our three-dimensional space) atoms will possess a close icosahedral configuration. In other words, in hardened alloy  $\text{Al}_{86}\text{Mn}_{14}$ , atoms are lined up to form the three-dimensional pattern of a six-dimensional ideal crystal which is advantageous in terms of energy because of the close icosahedral order. This model of the structure of an icosahedral quasicrystal makes it possible to rather successfully reproduce the diffraction pattern observed, as well as to calculate its physical properties.

As already noted, areas of an icosahedral order, regardless how large, are ultimately disrupted by defects which play an important role in formation of many glass properties. Topological analysis of atomic packets shows that the most interesting potential defects are those in the form of lines. These linear defects must either begin and end on the body's surface or be closed into rings. Moreover, it is very difficult for these lines to intersect one another. It is precisely this last factor which makes it possible to consider a clump of tangled linear defects as the model of the structure of a supercooled liquid.

One might imagine that the structure of a "hot" liquid (near melting point) is saturated with defects. As it cools, these defects are partially eliminated, but at a certain temperature thermal motion is not intense enough for further transformation of a clump of tangled defect lines, and it does not freeze in a vitreous state. This freezing occurs near the so-called vitrification temperature, when the viscosity of the supercooled liquid



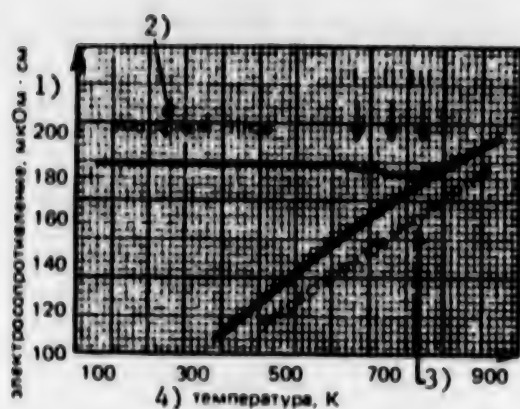
"Ring" formed by five tetrahedra with a common edge. An angle of  $7.5^\circ$  is needed to close the ring. Therefore, a structure comprising these atomic tetrahedra will contain rings of four and six tetrahedra. The common edge of these "anomalous" rings is a segment of a defect line.

increases very abruptly to high levels. Nevertheless, as a result of the high density of these defects, together with the difficulty of mutual intersection, most of the system's degrees of freedom turn out to be linked even more strictly than in an ideal crystal.

#### Special Properties at Superlow Temperatures

The concept of the structure of vitreous metal, like that of the system of tangled defect lines, helps us understand another class of interesting and unusual phenomena occurring in glass (metallic and dielectric) near absolute zero temperature. As much experimental data shows, between 0.01 and 1 K, specific heating capacity, thermal conductivity, speed and sound wave damping factor behave anomalously. For example, heating capacity rises in proportion to a first-stage temperature, not a third, as in crystals; the speed of sound is described by an unusual logarithmic function  $v_s \sim \ln T$ . The low temperatures at which these phenomena are in play make one think that they are caused by the quantum-mechanical tunnel movement of atoms or even whole groups of atoms. It is assumed that certain atoms near defect lines may be found in two close, almost equivalent configurations separated by a barrier of potential energy. Although the intensity of thermal motion at very low temperatures is insufficient to allow them to jump this barrier, quantum-mechanical tunneling ensures a small, but greater than zero, probability of shifts between two such configurations.

These atomic groupings, called two-level systems, interact with sound waves, conduction electrons, and other glass "exciters," causing the observed changes in their properties. Comparison of the calculated and the observed physical properties of glass has made it possible to evaluate the density of two-level systems, the height of the potential barriers, and other parameters which describe atomic structure. For example, it turned out that an average of only one atom per million belongs to two-level systems. However, this is sufficient to bring about qualitative changes in heating capacity, sound damping, electrical conductivity, and other parameters. Thus, study of low-temperature anomalies helps us understand the nature of complex phenomena which occur in a liquid near vitrification temperature (at  $300-400^\circ\text{C}$ ), when the amorphous structure itself forms.



Key:

- 1) Electrical resistance, microhms/centimeter
- 2) Amorphous alloy

Temperature dependence of the electrical resistance of a commercial amorphous alloy,  $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$  (as per K. V. Rao, *Amorphous Metallic Alloys*, Butterworth, 1983, pp. 401-421). In an amorphous state resistance is high and almost constant until the beginning of crystallization, which takes place in three stages (I, II, III). In a crystallized alloy, electrical resistance quickly drops with temperature reduction.

- 3) Crystallized alloy
- 4) Temperature, K

### The Poorest Conductors of Electrical Current

The electrical resistance of ordinary crystalline metals depends primarily on the dispersion of conduction electrons due to the shift of ions from equilibrium positions as a result of thermal vibrations. The amplitude of these shifts monotonically increases with a rise in temperature, but even near the melting point it is usually no more than 10 percent of the atomic spacing. Specific electrical resistance correspondingly increases in proportion to temperature and increases several times from room temperature to the melting point, reaching several tens of microhms per centimeter. Only certain highly resistive alloys have a resistance near 100 microhms/centimeter. The electrical resistance of many amorphous alloys behaves entirely differently. Even at temperatures far below room it is 150-200 microhms per centimeter or more. As temperature rises, it often does not increase, but rather drops sharply. After an amorphous alloy crystallizes, resistance resumes behavior typical for a crystalline condition.

Comparison of the amount of specific electrical resistance and its temperature dependence for numerous alloys (both amorphous and crystalline) has made it possible to derive a certain principle called the Mudge relation: the higher the resistance, the more slowly it increases with temperature. If resistance becomes higher than 150 microhms per centimeter, it drops as temperature rises. The Mudge relation thus means that, as temperature rises, ALL metals tend toward a limiting electrical resistance on the order of 150-200 microhms per centimeter. This ratio is universal--it is valid for all metals of the most varied types (alkaline, noble, transition, etc.). Therefore, its origin is related not to the unique features of electron structure, but probably to either atomic disorder or the specifics of the interaction of electrons with lattice vibrations. Existing theories have difficulty giving a clear-cut explanation to this universal behavior of metals, and not just because we still do not have a clear picture of the atomic structure of strongly disordered alloys (liquid, amorphous). The fact is that, at



maximum electrical resistance, effects typical not so much of metals as of dielectrics begin to be seen.

#### Amorphous Alloys — Valuable Magnetically Soft Materials

The combination of high electrical resistance and ferromagnetic properties provides a basis for the numerous applications of alloys in technology which we mentioned at the beginning of the article. The very possibility of ferromagnetism in the absence of a crystal lattice long seemed unrealistic. This possibility was theoretically predicted for the first time in a work by A. I. Gubanov and was confirmed experimentally several years later.<sup>6</sup> We now know many alloys which contain transition or rare-earth metals which become magnetic below a certain temperature (Curie temperature). The basic physical characteristics of magnetic materials — atomic magnetic moment ( $\mu_B$ ) and Curie temperature ( $T_C$ ) are usually somewhat lower than in crystalline alloys of similar composition. Since glass crystallizes when heated, one can observe a curious phenomenon: a sample becomes demagnetized twice—once in an amorphous state, and then having become magnetic, again after crystallization, at the Curie "crystalline" point.

In view of the technical applications of ferromagnetic materials, certain requirements must be imposed not only on  $\mu_B$  and  $T_C$ , but also on the characteristics of the process of sample magnetization in an external field. As already mentioned, the specific nature of amorphous structure as compared with crystalline is in its homogeneity: there is no rectilinear lattice, but there are no defects which abruptly disrupt the atomic order. This homogeneity is important from the standpoint of magnetization processes, since the movement of magnetic domain boundaries (segments of magnetic materials magnetized in one direction) greatly depends on their interaction with structure heterogeneities. Although internal stresses, fluctuations in composition and density, and the ordered arrangement of atomic pairs result in highly heterogeneous magnetic properties and formation of a specific domain structure similar to a labyrinth, magnetization parameters still remain quite high, at least as compared with mass-produced electrotechnical steels.

Alloy Fe-B in an amorphous state possesses one other very interesting and valuable property: with a 17-percent boron content, this alloy's thermal expansion is almost nil over a wide range of temperatures. This anomaly, call invar, is known in certain crystalline alloys (Fe-Ni, Fe-Pd). It is due to the competition between ordinary thermal expansion and magnetostriction (i.e. the change in volume when a magnetic order is established) near the Curie point. A similar situation probably occurs also in this amorphous alloy, but there is no final theory on the phenomenon in either case.

#### Strength, Ductility, Corrosion Resistance

Vitreous metals' lack of a crystalline structure and the defects inherent in it, particularly dislocation, have presented metals physicists studying the



mechanical properties of alloys with very difficult problems.

How does plastic flow of a glass occur without dislocation?! We have already said that an amorphous substance near vitrification temperature is a very viscous fluid. Exposed to external load, it flows, i.e. particle displacements are distributed more or less uniformly through the body's volume. As temperature drops, when the glass becomes solid, the homogeneous flow is replaced by plastic deformation. If the load is sufficiently high, then the material deforms because "slip bands" form and develop, as in a crystal. However, while slip bands in crystalline metals are places where dislocations move along atomic planes, this pattern is disturbed in an amorphous state. Experience shows that irreversible changes in atomic structure take place within the bands, but their microscopic nature remains unclear.

Because the stress at which a heterogeneous laminar deformation begins depends little on temperature forces, we must assume that flow is transferred by some sort of structural elements which, like dislocations, are present in a sample from the very beginning, but do not result from deformation or heating. It is possible that the very linear defects which we discussed when we talked about atomic structure serve as these structural elements. Whatever they are, the specific nature of plastic deformation mechanisms in vitreous metals make their strength close to the theoretically permissible limit for ideal defect-free crystals. Record-breaking strength, considerable ductility, low sound wave attenuation — this is an incomplete list of advantages of amorphous alloys in terms of their mechanical behavior. These properties may be used in the most diverse goods and devices: from acoustic delay lines to tires.

Concluding our very brief description of the properties of vitreous metals, we will spend a little time on their resistance to aggressive media, i.e. corrosion. It was discovered that certain alloys, especially  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  possess tremendous resistance to the effects of these substances, in which ordinary stainless steel is rapidly destroyed (sulfuric acid,  $\text{NaCl}$  and  $\text{FeCl}_3$  solutions). Comprehensive studies of this phenomenon conducted primarily by Japanese scientists showed that the corrosion resistance of these amorphous alloys, like similar crystalline alloys, results from formation of a thin layer of chemical compounds (a passivating layer, as it is called) on their surfaces which comes in contact with the aggressive medium. This layer protects the main mass of the metal from further damage. The chemical composition of these layers, containing oxy-hydroxides of chrome, turned out to be close to that of the passivating layers on crystalline metals. However, small quantitative differences, along with high structure uniformity, apparently provide very reliable surface protection against destruction. Attempts are already being made to use corrosion-resistant metallic glasses as filters in chemical production, as well as catalysts for chemical reactions. High corrosion resistance, combined with hardness, strength, and wear resistance, make amorphous metals an ideal material for razor blades — they last considerably longer than do platinum steel blades. Considering that razor blades are used by almost

half of mankind, it is easy to imagine the economic benefits to be realized from introduction of vitreous metals in this application alone.

As a result of 25 years' research, it has been possible to create an actually new class of materials with a unique combination of physical and technological properties — amorphous alloys, which grow in number every year. At the same time, a new page has been turned in physical metallurgy, which has been enriched by new and sometimes quite unexpected ideas and facts.

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12809

CSO: 1842/98

## PROPERTIES OF Ni MODIFIED BY IMPLANTATION OF Ag IONS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6,  
Nov-Dec 86 (manuscript received 4 Jun 86) pp 9-14

[Article by I. S. Tashlykov, Ye. B. Boyko, O. A. Slesarenko  
and F. F. Komarov, Minsk]

[Abstract] An experimental study of Ni anodes with implanted Ag ions increasing their surface activity was made, both polycrystalline Ni and single crystals with (110\_ orientation being considered. Implantation was done at room temperature with 40-50 keV ions in doses of  $10^{14}$ - $1.1 \cdot 10^{17}$  cm<sup>-2</sup>. The ion current was varied over the 0.5-3  $\mu$ A/cm<sup>2</sup> range in polycrystalline Ni and over the 3-5 mA/cm<sup>2</sup> range in single crystals. Activity involving O<sub>2</sub> evolution in aqueous 30% KOH solution at a temperature of 80°C was measured in the galvanostatic mode with a current density of 0.2 A/cm<sup>2</sup> and on the basis of stationary polarization curves. Electrocatalytic activity involving O<sub>2</sub> ionization in 1 N KOH solution at a temperature of 25°C was measured by the potentiodynamic method with a 0.3 mV/s<sup>-1</sup> sweep, using a Ni auxiliary electrode and a H<sub>2</sub> reference electrode. Oxidation in 1 N KOH solution at a temperature of 20°C was measured on the basis of polarization curves plotted by the potentiodynamic method with a 10 mV/s<sup>-1</sup> sweep from -0.2 V to +1.55 V with respect to a standard H<sub>2</sub> electrode. An evaluation of the data has yielded the distributions and the energy spectra of implanted Ag ions and backscattered He ions as well as the composition of the Ni surface and the electrochemical characteristics of Ni after implantation of Ag ions. Anodic oxidation of such Ni is attributable to preferential migration of Ni atoms to the surface through the original oxide film in which now containing Ag atoms. Reference 17: 7 Russian, 10 Western.

2415/12223  
CSO: 1842/82

**EXPERIMENTAL CRYSTALLIZATION OF ALUMINUM MELTS IN  
'EVAPORATOR-M' APPARATUS**

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6,  
Nov-Dec 86 (manuscript received 29 May 86) pp 41-46

[Article by V. N. Pimenov, V. F. Shulym, S. A. Maslyayev and  
S. Ya. Betsofen, Moscow]

[Abstract] Series of crystallization experiments with melts of pure Al and of Al+ 0.2 wt.% Cu alloy in the "Evaporator-M" apparatus had been designed for eventual application in space technology, their purpose being to study the grain orientation along the temperature gradient in specimens grown vertically (temperature gradient parallel to gravitation vector) and in specimens grown horizontally (temperature gradient perpendicular to gravitation vector). The first series of experiments was performed on earth, the "Evaporator-M" apparatus having been used before in the Soviet-Indian "subcooling" experiment. The apparatus consists of a Mo radiation source in the form of a hemicylindrical shell inside a cylindrical container, heated on the convex side by a defocused electron beam entering through a hole in the container till it emits infrared radiation on the concave side. This radiation heats and melts the target material in a graphite crucible under a lid inside a quartz tube placed on the focal line of the heater. For subsequent crystallization, heat is drawn away from the focal zone through a hole in vacuum-shield insulation at a controlled rate ensuring the necessary temperature gradient of approximately 10 C/cm along the heater axis. The experiments were performed with Al and Al+ 0.2% Cu specimens in the form of solid cylinders 2 cm long and 0.6 cm in diameter. Crystallization from the center toward both ends of the melt was monitored on the basis of subsequent X-ray structural examination by the Laue method, after solidification, in three representative cross-section including one cut through the center. Evaluation of these data, theoretical analysis of heat transfer by diffusion and by Rayleigh convection as well as by the Marangoni thermocapillary effect, and theoretical analysis of mass



transfer taking into account surface tension during crystal growth with an f.c.c. lattice indicate a grain orientation  $\langle 100 \rangle // \text{grad } T$  only in vertically grown specimens. Absence of preferential grain orientation in horizontally grown specimens is attributed to the Marangoni thermocapillary effect, which alters the temperature field and turbulizes the melt flow so that solidification occurs spontaneously at random. The distribution of Cu in alloy crystals was found to be the same in vertically and horizontally grown specimens. References 15: 11 Russian, 4 Western (2 in Russian translation).

2415/12223

CSO: 1842/80

UDC 536.421.4+531.5

COMPENSATION OF MARANGONI THERMOCAPILLARY EFFECT DURING  
DIRECTIONAL CRYSTALLIZATION UNDER MICROGRAVITY

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6,  
Nov-Dec 86 (manuscript received 2 Jul 86) pp 47-52

[Article by V. N. Pimenov, Moscow]

[Abstract] A problem of "contactless" directional crystallization under microgravity is considered, namely compensation of Marangoni thermocapillary flow owing to the temperature dependence of surface tension by concentrational capillary flow due to the concentration dependence of surface tension. The condition for such a compensation is established on the basis of the corresponding Navier-Stokes vector equation of hydrodynamics for an incompressible fluid in absence of gravity and associated body forces in which "ideal" case the gradient of surface tension is the only force driving the fluid, the surface tension being generally a function of both concentration and temperature. An analysis of these relations indicates that hydrostatic equilibrium will prevail as long as the thermocapillary effect dependent on the longitudinal concentration profile. This principle can serve as basis for conducting crystallization experiments in space if equilibrium can be maintained throughout the process of crystal growth by the Bridgman-Stokbarger method with high cooling rate under residual gravitational acceleration  $g \leq 10^{-4} g_0$  ( $g_0$  gravitational acceleration on earth).  
References 14: 12 Russian, 2 Western (both in Russian translation).

2415/12223

CSO: 1842/82

**EFFECT OF PLASMA ARC MODULATION ON ADHESION AND GAS-PERMEABILITY OF POWDER COATINGS**

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, in Russian No 6, Nov-Dec 86 (manuscript received 9 Jul 86) pp 61-64

[Article by B. Ye. Gutman and M. Kh. Shorshorov, Moscow]

[Abstract] An experimental study of powder coating deposition on steel with a plasmatron was made for the purpose of establishing the advantage of plasma arc modulation and confirming the advantage of the addition of propane-butane gas to plasma generating pure air. Specimens of St40 steel were coated with P-Ni55Ti45 alloy powder, its grain size distribution covering a range as wide as 5-150  $\mu\text{m}$ . Coating was done with a 30 kW EDP-104 plasmatron using a self-sustained arc of stable length,  $1.1 \cdot 10^{-2}$ - $17.10^{-2}$   $\text{m}^3/\text{s}$  propane-butane gas being added to  $1.1 \cdot 10^{-2}$   $\text{m}^3/\text{s}$  air, the theoretical velocity of air plasma flow being 400 m/s and the spray distance being maintained at 160 mm. The plasma arc was modulated by subtraction of currents, a subtraction pulse having an amplitude of -720 A and a duration of 6  $\mu\text{s}$ . Voltage maxima occurred at modulation frequencies of 300, 1300, 2800, 4200 Hz, the increment of average voltage reaching a maximum of +20 V with the average current dropping to -20 A at the modulation frequencies of 2800 Hz and 4200 Hz. Addition of propane-butane gas already contributes to a higher enthalpy of the plasma stream, to a better process economy, and to controllability of the plasma medium over a wide range from an oxidizing to a reducing one. Measurements of powder grain size and velocity, coating thickness, hardness, and adhesion strength, also chemical analysis of the plasma by gas chromatography, indicate that modulation of the plasma arc at a sufficiently high frequency can significantly increase the adhesion and use factor of the powder and reduce the gas permeability of plasma powder coatings. References 3: 2 Russian, 1 Western (in Russian).

2415/12223

CSO: 1842/78

**EFFECTIVENESS OF COMPACTING POWDERS OF BB-Cr15 BALL-BEARING STEEL BY HOT EXTRUSION**

Kiev POROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87  
(manuscript received 13 Feb 86) pp 25-28

[Article by Yu. L. Krasulin (deceased), N. V. Abashkina, V. S. Ivanov, F. R. Karelin and B. F. Sherayzin, Metallurgy Institute, UkSSR Academy of Sciences]

[Abstract] The feasibility of compacting steel powders by hot extrusion, and thus principally during the deformation process, is evaluated theoretically on the basis of applicable relations, experiments having been performed with powders of BB-Cr15 ball-bearing steel. Density and porosity, yield strength and ultimate strength, also percentage elongation of compacts were measured as functions of the draw factor, as well as the dependence of the grain size on the draw factor. After extrusion, specimens were annealed to Brinell hardness of 2200/Nmm<sup>2</sup> for subsequent heat treatment by quenching from 830°C (45 min) in oil and tempering with the temperature raised at a rate of 160°/h. Noteworthy is the high yield strength, which consistently increases as the draw factor increases from 1.53 (18% deformation) to 2.15 (33% deformation) and further to 10.3, although less so after annealing. References 9: 8 Russian, 1 Western (in Russian translation).

2415/12223

CSO: 1842/78



LIQUID-PHASE SINTERING OF HIGH-DENSITY COMPACTS FROM  
PREPULVERIZED ALUMINUM ALLOYS

Kiev PROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87  
(manuscript received 27 May 86) pp 29-34

[Article by V. A. Vasilyev, B. S. Mitin and M. M. Serov,  
Aviation Technological Institute, Moscow]

[Abstract] Powders of the Al+ 5 wt.% Cu alloy were experimentally liquid-phase sintered after cold alloy powder had been heated to temperatures within the approximately 80°C wide solidus-liquidus range, the amount of liquid phase during sintering thus being easily controllable. Cold alloy powders were produced by high-speed solidification of the melt, a thin layer at a time, on a disk rotating at a constant speed and making contact with the melt surface. metallographic examination and X-ray phase analysis revealed a breakup of alloy particles with a redistribution of Cu grains and formation of free  $Al_2O_3$ . They also revealed a shrinkage of the surface, which correlates with changes in the free energy during phase transformation and contributes to breakdown of the  $Al_2O_3$  film and its dispersion in the melt so that metallic contacts form and the mechanical strength of the compact increases. References 5: 4 Russian, 1 Western (in Russian translation).

2415/12223  
CSO: 1842/78

UDC 661.55:621.762.4:620.178

STRUCTURE OF HOT-PRESSED MATERIALS CONSISTING OF SIALON AND  
REFRACTORY COMPOUND

Kiev POROSHKOVAYA METALLURGIYA in Russian No 1, Jan 87  
(manuscript received 26 Jan 85) pp 45-48

[Article by O. V. Bakun, O. N. Grigoryev, G. G. Gnesin, Yu. N. Ivashchenko, V. V. Kovylyayev, I. I. Osipova, V. I. Trefilov, S. A. Firstov and V. P. Yaroshenko, Institute of Materials Science Problems, UkSSR Academy of Sciences]

[Abstract] An experimental study of sialon powder ceramics was made for an evaluation of their structural characteristics acquired during hot pressing in order to determine their suitability as construction and tool materials with adequate mechanical properties. A mixture of  $\text{Si}_3\text{N}_4$  + 21.4 wt.%  $\text{Al}_2\text{O}_3$  + 11.6 wt.%  $\text{AlN}$  powders with (10-90)%  $\text{TiN}$  was selected as model material, other materials under consideration being  $\text{Si}_3\text{N}_4$  + 5 wt.%  $\text{Al}_2\text{O}_3$  with (7-40)%  $\text{TiC}$  and  $\text{TiN}$  + (10-80)%  $\text{BN}$ . Pulverization, hot pressing, and sintering were monitored for grain structurization and phase transformations depending on the process temperature and the processing time. Data were thus obtained supplementing the respective constitution diagrams. Specimens of ceramics produced were tested mechanically. The results indicate an appreciable solid-solution dispersion hardening at temperatures of 300-1300 K, prior to hot pressing at 2050 K or higher temperature, and microcracking with formation of high-strength low-stress interphase boundaries after intense chemical reactions, all this contributing to a higher mechanical strength of the product. References 5: 4 Russian, 1 Western.

2415/12223

CSO: 1842/78

EFFECT OF LASER TREATMENT ON STRUCTURE AND COMPOSITION OF  
PLASMA-DEPOSITED Ni-Cr-Si-B COATINGS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 1,  
Jan-Feb 87 (manuscript received 10 Jul 86) pp 73-77

[Article by V. P. Larionov, N. P. Bolotina, T. V. Argunova,  
V.D. Tyunin and M. P. Lebedev, Yakutsk]

[Abstract] An experimental study of plasma-deposited coatings and their treatment with a CO<sub>2</sub>-laser was made, the purpose of such a treatment being to strengthen their adhesion. Coatings 0.3-0.4 mm thick were deposited from Ni-Cr-Si-B mining grade PGSR-4 powder by means of a standard UPU-ZD plasmatron with GNP-005/23 interelectrode inserts using nitrogen as the plasma generating gas. They were subsequently treated with a continuous-wave CO<sub>2</sub>-laser at three power levels; 1.9-1.5-1.2 kW. Metallographic examination under a "Neophot-21" microscope, phase analysis in a DRON-1.5 X-ray diffractometer, X-ray spectral microanalysis with a "Cameca MS-46" analyzer, and microhardness measurements with a MPT-3 tester revealed a dependence of coating structure and composition on the mode of laser treatment. Prior to treatment the coatings constituted a Ni-base solid solution with hardening phases CrB, Cr<sub>7</sub>C<sub>3</sub> and Ni<sub>2</sub>Si. Treatment at the highest power level resulted in formation of  $\alpha$ -Fe along with FeB and Cr<sub>23</sub>C<sub>6</sub>. Treatment at the intermediate power level resulted in formation of  $\alpha$ -Fe along with Cr<sub>3</sub>C<sub>2</sub> and more Cr<sub>7</sub>C<sub>3</sub>. Treatment at the lowest power level resulted in formation of metallic Ni along with Cr<sub>23</sub>C<sub>6</sub> and more Cr<sub>7</sub>C<sub>3</sub>. The special trigonal carbide Cr<sub>7</sub>C<sub>3</sub>, forming in coatings with 2-8% Cr content, has been found to be the principal hardening phase and to impart a high wear resistance to the coatings. Laser treatment thus evidently improves the mechanical characteristics of Ni-Cr-Si-B coatings. References 6: all Russian.

2415/12223

CSO: 1842/93

UDC 669.1+669.71:533.9

COMPOSITION OF Fe-C AND Al-Si SURFACE LAYERS AFTER CONTACT  
WITH PLASMA AND SPUTTERING PRODUCTS

Moscow FIZIKI I KHIMIYA OBRABOTKI MATERIALOV in Russian No 1,  
Jan-Feb 87 (manuscript received 31 Oct 85) pp 84-88

[Article by N. V. Popova, C. B. Bukelich and Ye. G. Popov,  
Dnepropetrovsk]

[Abstract] The effect of plasma-sputtering treatment on the chemical composition of the surface layers of ferrous alloys and silumin alloys was examined by the method of X-ray spectral microanalysis. Silumins for this study were produced from spectrally pure Al and semiconductor-grade Si. Ferrous alloys for this study included Armco iron, gray cast iron, white cast iron, malleable cast iron, plain carbon steels St10/20/35/45, Cr18Ni9Ti stainless steel, and 4CrSi tool steel. Strips of each material were stacked for treatment in a shock tube with pulses of a high-density plasma under a pressure of 0.7 GPa for a duration of 0.3 ms, pulses of an air or N plasma at a temperature of  $2 \cdot 10^4$  K or of an Ar plasma at a temperature of  $3.8 \cdot 10^4$  K. The distributions of elements C, N, Al, Si, P, S, Ti, Cr, Mn, Ni, Cu, Mo and Ce were determined on the basis of  $K\alpha$ -lines in the X-ray spectra, with "Cameca" Camebax and MS-46 microanalyzers. Corrections for atomic number, radiation absorption, and fluorescence were calculated on a HP 9835A minicomputer according to the RUST program. The results indicate an increase of C, Si, Cr, Ni in ferrous alloys and an increase of Fe in silumin alloys, not only uniformly within the surface layer but also deeper below, evidently caused by interaction with the plasma and with the sputtering products as well as by mass transfer from the tube walls made of Cr18Ni10Ti. References 13: all Russian.

2415/12223  
CSO: 1842/93



## FEASIBILITY OF PRODUCING FINE-DISPERSE COMPOSITE MATERIALS IN PULSED HIGH-ENTHALPY STREAM

Moscow FIZIKA I KHIMKIYA OBRABOTKI MATERIALOV in Russian No 1, Jan-Feb 87 (manuscript received 6 Jun 86) pp 111-115

[Article by I. V. Blinkov, A. G. Brodyagin and A. V. Ivanov, Moscow]

[Abstract] The feasibility for producing fine-disperse heat-resistant Mo-TiC powder alloys by coreduction of  $TiCl_4$  and  $MoCl_5$  in a stream of  $CH_4-H_2$  plasma is examined on the basis of theoretical analysis of the Ti-Mo-C-H-Cl system thermodynamics and a practical experiment. Calculations were made according to the ASTRA program H:Cl=1-200 and C:Ti=0.5-1.5 ratios and the 100-4000 K temperature range at atmospheric pressure, with formation of solid solutions disregarded and with the relative amounts of H, Cl, C and Ti matched for a Mo-TiC material with a Mo:TiC=9:1 ratio ensuring maximum heat resistance. The experiment was performed in plasmochemical reactor operating in the pulse mode,  $MoCl_5$  vapor being transported by an argon stream from the evaporator through the hollow center electrode into the discharge space and  $TiCl_4$  vapor being fed into the reaction space by bubbling  $CH_4$  through liquid  $TiCl_4$ . Gravimetric analysis of the coreduction products for loss of evolving gases in a "DuPont-1090" thermoanalyzer revealed a 40% total loss of mass after complete coreduction, attainable with a 1.5 kJ discharge energy and with H:Cl=90 and C:Ti=1.1 ratios. Phase analysis in a "Geigerfleh" X-ray diffractometer and X-ray spectral microanalysis under a "Jeol" scanning electron microscope revealed in this case a highly homogeneous fine-disperse composite powder in the 10 nm grain size fraction without lower chlorides. References 7: 6 Russian, 1 Western.

2415/12223

CSO: 1842/93

## PRODUCTION AND EXAMINATION OF AMORPHOUS Zr ALLOYS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 1, Jan-Feb 87 (manuscript received 13 Feb 86) pp 124-127

[Article by I. A. Tregubov, L. N. Yevseyeva and S. B. Maslennikov, Moscow]

[Abstract] Ternary amorphous Zr-Fe alloys with addition of any of the elements Ni, Cu, Nb, Mo and Sn were produced by ultrafast quenching of the melt on a heavy copper disk rotating at a high speed of 2700 rpm, plain binary amorphous Zr-Fe alloys not having sufficient thermal stability. The degree of amorphization was monitored on low-angle x-radiograms revealing only one diffuse annular "halo", while crystallization was indicated by appearance of distinct lines. Seven such alloys were studied (atom.%): Zr + 19.1 Fe + 19.3 Ni, Zr + 20.7 Fe + 15.3 Cu, Zr + 21.4 Fe + 15.6 Cu, Zr + 24.0 Fe + 0.8 Nb, Zr + 23.3 Fe + 1.8 Nb, Zr + 24.0 Fe + 3.3 Mo and Zr + 23.8 Fe + 1.3 Sn. Ribbons of these alloys 0.03 mm thick and 3-4 mm wide were found to be highly plastic in flexure, their microhardness measured with a diamond indenter being the same as that of crystalline ones. Tensile tests performed on 20 mm gage-long specimens under a uniaxial load in an "Instron" machine revealed intense elastic deformation by shear prior to fracture, either brittle fracture after localization of cracks and their propagation in the direction of maximum stress or ductile fracture after shear flow spreading over the entire cross-section. For a study of the crystallization kinetics, specimens were held at a temperature of 350 C for 10-2000 min under vacuum, to prevent oxidation, and then examined at room temperature. The results of X-ray phase analysis indicate a thermal stability ranging from 30 min (Zr + 20.7 Fe + 15.3 Cu) to 1800 min (Zr + 21.4 Fe + 15.6 Cu) at that temperature. References 9: 4 Russian, 5 Western (1 in Russian).

2415/12223  
CSO: 1842/93

ELECTRICAL-CONTACT ALLOYING OF STEEL SURFACE WITH FIBROUS CARBON

Moscow SVAROCHNOYE PROIZVODSTVO in Russian No 2, Feb 87 pp 10-11

[Article by V. G. Syvynyuk, engineer, A. A. Zhukov, doctor of technical sciences, and A. M. Zarechnyy, candidate of technical sciences, Vinnitsa Polytechnical Institute]

[Abstract] Surface carburization of low-carbon steel with microfibrous disperse carbon by the electrical-contact method was done experimentally, the purpose being the refinement of this technology. The advantages of this method are fast heating to high temperatures and subsequent fast flashing. The advantages of fibrous disperse carbon over graphite are its excellent wettability by liquid steel, which facilitates fast conversion of the latter into a high-carbon steel or white cast iron melt, and its solubility in liquid steel without formation of graphitization centers even when the  $\text{Fe}_3\text{C}$  content is high. An 0.8 mm thick disk of fibrous carbon (density 0.2 kg/m<sup>2</sup>, mass 0.15 g) 25 mm in diameter was placed on an 8 mm thick plate of St3 steel free of scale and pressed to it by a cylindrical copper electrode 20 mm in diameter. A current pulse of 13 kA magnitude and 1 s duration from a 3.2 V source heated the carbon disk to 2000°C, below the sublimation point, the pulse being sufficiently short to minimize oxidation of carbon in air. Microstructural examination revealed formation of an adequately thick case. metal cutting tools made of St45 carbon steel surface-alloyed with carbon as well as with tungsten or titanium by this method were found to rank in performance between tools made of high-speed steels and tools made of hard alloys. References 2: In Russian.

2415/12223

CSO: 1842/80

RATE OF MELTING OF TITANIUM IN MELT OF STAINLESS STEEL

Moscow IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: CHERNAYA  
METALLURGIYA in Russian No 2, Feb 87 (manuscript received  
4 May 86) pp 35-39

[Article by V. A. Golubtsev, A. S. Noskov, A. L. Zavyalov,  
V.I. Zhuchkov, V. G. Pavlov and G. F. Gladyshev, Metallurgy  
Institute, Ural Scientific Center, USSR Academy of Sciences,  
Sverdlovsk]

[Abstract] Alloying stainless steels (8-12)Cr18Ni(9-10)  
containing 0.08-0.12% C with titanium is examined for  
optimization purposes, chips or lumps of ferrotitanium with a  
melting point higher than that of steel being added to the  
melt during casting rather than during smelting in an  
electric-arc furnace. Assimilation of ferrotitanium in the  
Fe-C melt during casting occurs in two stages, first steel  
solidifying on the Ti surface during the thermal stage and  
then Ti dissolving in the steel crust during the diffusion  
stage. Theoretical analysis on the basis of an analogy  
between heat transfer and mass transfer, according to a  
mathematical model of the process kinetics in the quasi-steady  
approximation with the effects of natural and forced  
convection being additive and aided by experimental data as  
well as thermophysical and other reference data, yields the  
duration of each stage and the rate of Ti melting-dissolution.  
The distribution of Ti in steel as cast and after forming was  
determined on the basis of X-ray spectral analysis. The  
results indicate an 85-90% assimilation of Ti and its much  
more uniform distribution after stirring of the melt when it  
has been added during casting, with only a 63-80% assimilation  
when it has been added during smelting. References 13: 9  
Russian, 4 Western (3 in Russian).

2415/12223  
CSO: 1842/94



CHARACTERISTICS OF LIQUID-PHASE SINTERING OF Mo-Cu  
PSEUDOALLOYS WITH BIPOROUS STRUCTURE

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 6 May 86) pp 36-39

[Article by L. I. Chernyshev, Institute of Materials Science  
Problems, UkSSR Academy of Sciences]

[Abstract] An experimental study of liquid-phase sintering of Mo-Cu powder pseudoalloys with a biporous structure was made for the purpose of determining the porosity spectrum and the gas permeability of the product. Disk specimens 6 mm thick and 20 mm in diameter were produced by liquid-phase sintering of compacts containing a mixture of Mo and Cu powders with a blowing agent, all of the 0.125-0.16 mm grain size fraction and the Cu content varied over the 20-50% range. With the initial porosity at the 70% level, final volume shrinkage, porosity, air permeability, and maximum pore dimension were measured after sintering at 900 K for 10-3600 s. The porosity spectrum revealed two pore fractions, macropores with a sharp high volume peak corresponding to the 40  $\mu$ m pore dimension and micropores with a softer lower volume peak corresponding to the 0.4  $\mu$ m pore dimension. A final porosity above 60% was found to be attainable by this sintering process with use of a volatile blowing agent. The results indicate that the structural characteristics of such a pseudoalloy product depend on the Cu content, volume shrinkage increasing and porosity decreasing but maximum pore dimension and air permeability also increasing as the Cu content increases till it exceeds the volume of micropores and the pseudoalloy structure becomes monoporous. References 5: all Russian.

2415/12223  
CSO: 1842/95

UDC 536.23:532.546:621.762.5

PROPERTIES OF POROUS W-Cu AND Mo-Cu PSEUDOALLOYS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 4 Feb 86) pp 47-50

[Article by A. V. Yegorov, A. G. Kostornov, V. A. Koshelev,  
G.N. Melnikov, A. V. Pustogarov, V. P. Semenets and  
L.I.Chernyshev, Institute of Materials Science Problems, UkSSR  
Academy of Sciences]

[Abstract] An experimental study of W+ (15-30)% Cu and Mo+ (27.2-36.8)% Cu pseudoalloys with 49-84% porosity was made for a determination their hydraulic resistance and heat transmission characteristics. Disk specimens 8-12 mm thick and 40 mm in diameter were produced by liquid-phase sintering at a temperature of 1500 K from mixtures of W and Cu or Mo and Cu powders with a volatile blowing agent. Their resistance to scaling was increased by chromium impregnation, with "active"  $\text{CrCl}_2$  generated by reaction of a metallic Cr charge and  $\text{H} + \text{HCl}$  gas. Both viscous and inertial components of the hydraulic resistance were determined graphoanalytically from curves representing the dependence of the pressure drop on the gas flow rate with the pressure drop not exceeding 3% of the applied pressure. The thermal conductivity was measured by the method of axial heat flow, with a disk facing on each side a thermocouple 2 mm away from it and embedded in In-Ga eutectic alloy. The coefficient of convective heat transfer was determined on the basis of the transient response to an aperiodic impinging heat wave. While both components of hydraulic resistance and the thermal conductivity were found to decrease monotonically with increasing porosity, the coefficient of convective heat transfer was found to peak at about 50% porosity. References 6: 5 Russian, 1 Western.

2415/12223  
CSO: 1842/95

HARDENING HEAT TREATMENT OF TITANIUM ALLOYS WITH RAPID  
HEATING

Moscow METALLOVEDENIYE I TERMICHESKAYA OBRABOTKA METALLOV in  
Russian No 3, Mar 87 pp 28-31

[Article by A. I. Gordiyenko, Physical Technical Institute,  
BSSR Academy of Sciences]

[Abstract] Ten titanium alloys containing various amounts of  $\beta$ -phase stabilizing elements were experimentally hardened by rapid electrothermal treatment for a comparative evaluation of its effectiveness. The effectiveness of such hardening was gauged by the difference between the ultimate tensile strength after regular heat treatment (quenching, annealing) and after subsequent electrothermal treatment respectively. Most effectively hardened ( $1400-1450 \text{ N/mm}^2$ ) with adequate retention of plasticity and with 30-60%  $\beta$ -phase stabilization were the martensitic alloys VT9 (6.3% Al, 3.2% Mo, 1.6% Nb) and VT3-1 (6.1% Al, 2.3% Mo, 1.6% Cr, 0.5% Fe) after quenching. Most effectively hardened ( $1450-1600 \text{ N/mm}^2$ ) after aging was the critical alloy VT22 (5.1% Al, 4.6% Mo, 1.1% Fe, 1.0% Cr). The strength of the near-critical alloys VT16 (5.3% Mo, 4.3% V, 2.4% Al, 0.3% Zr, 0.1% Fe) and VT23 (5.5% Al, 4.5% V, 2.3% Mo, 1.1% Cr, 0.5% Fe), quenched, became only  $150-200 \text{ N/mm}^2$  higher. References 10: all Russian.

2415/12223  
CSO: 1842/96

## TREATMENTS

UDC 669.87.15'778:537.3+539.1.04

### ELECTRICAL PROPERTIES OF InAs AFTER BOMBARDMENT BY FAST NEUTRONS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6, Nov-Dec 86 (manuscript received 4 Feb 86) pp 3-8

[Article by N. G. Kolin, V. B. Osvenskiy, N. S. Rytova and Ye. S. Yurova, Moscow]

[Abstract] In an experimental study single crystals of intrinsic InAs and of InAs doped with Pb or Zn to various levels were bombarded with fast neutrons for the purpose of determining the effect of such a bombardment on the electrical properties of these semiconductor materials. Single crystals were grown by the Czochralski method, with a resulting dislocation density of  $\sim 10^4 \text{ cm}^{-2}$ , and then bombarded with neutrons of energy higher than 0.3 MeV at an intensity of  $5.10^{12} \text{ cm}^{-2} \cdot \text{s}^{-1}$  in vertical channels of a VVR-Ts water-moderated water-cooled reactor at a temperature not higher than  $70^\circ\text{C}$ . The fluence of fast neutrons was varied over the  $5.10^{15} - 5.10^{18} \text{ cm}^{-2}$  range, while the thermal neutron flux was attenuated by means of 1 mm thick Cd shields so as to exceed 10% of the fast neutron flux. An evaluation of the experimental data on the basis of applicable theory has yielded the dependence of the charge carrier concentration in InAs on the neutron fluence and on the doping level at room temperature. After annealing at temperatures up to  $900^\circ\text{C}$  the dependence of the charge carrier concentration and mobility at various doping and neutron fluence levels on the annealing temperature was established. The results indicate that these electrical properties are determined by donor-acceptor interaction, especially during high-temperature heat treatment. The maximum electron concentration attainable at high neutron fluence levels depends on the ratio of probabilities of donor defect and acceptor defect formation. Annealing of defects is found to be most effective at temperatures within the  $300 - 600^\circ\text{C}$  range but, while donor defects become almost completely cured, acceptor defects do not and many of them remain even



after annealing at  $900^{\circ}\text{C}$ . For any annealing temperature there is a doping threshold level above which the concentration of residual acceptor defect will begin to increase with increasing doping level. References 4: all Russian.

2415/12223  
CSO: 1842/82

UDC 535.241.4

ENERGY LOSSES BY REFLECTION DURING TREATMENT OF MATERIALS WITH  
HIGH-POWER LASER RADIATION

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6,  
Nov-Dec 86 (manuscript received 25 Jul 85) pp 18-23

[Article by A. I. Skripchenko, V. N. Smirnov and  
S. V. Grigoryev, Leningrad]

[Abstract] A problem in laser treatment of metals is considered, namely reflection of laser radiation by the metal which is particularly appreciable at power density levels approaching the vapor-gas funneling threshold. The resulting energy loss is evaluated on the basis of an experiment and applicable theoretical relations. The experiment was performed with a power laser and an optical focusing system. A spot 0.4 mm in diameter with  $1 \text{ MW/cm}^2$  at the center and  $0.5 \text{ MW/cm}^2$  at the periphery was produced at a  $7^\circ$  angle on the  $60 \times 200 \text{ mm}^2$  large surface of 10 mm thick specimens of 08Cr18Ni10Ti alloy steel, with the interaction region shielded by gaseous He. A tungsten wire 30  $\mu\text{m}$  in diameter parallel to the specimen surface at a distance of 60 mm from it served as receiver of reflected radiation, with a shield behind it, converting radiation to electric signals while the laser beam was modulated mechanically by rotating disk with holes at frequencies covering the 80-250 Hz range. The specimen was moved parallel to the tungsten wire for linear scan. This arrangement had been designed to eliminate interference from heat emission by the specimen and heat convection in air streams. The electric signal from the receiver was, after passage through an amplifier, demodulated by a detector and rectifier. The results of the experiment are analyzed in terms of geometrical and energy relations in a spherical system of coordinates, assuming a linear response characteristic of the radiation receiver. The reflection pattern is calculated, its width and peaks depending on both peak and average laser radiation power as well as on the modulation frequency. The experiment and the analysis reveal the mechanism of vapor-gas funneling in molten metal, namely

that transition from pure surface heating to such funneling occurs within an intermediate range of laser power and is accompanied by a steep drop of the reflection coefficient to below 20% with the reflection pattern approaching Lambert's law. References 5: 4 Russian, 1 Western.

2415/12223

CSO: 1842/82

UDC 669.794:539.1.043

CROSS-SECTION FOR FORMATION OF RECOIL ATOMS UNDER BOMBARDMENT  
BY 21 MeV ELECTRONS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6,  
Nov-Dec 86 (manuscript received 21 May 86) PP 125-126

[Article by V. P. Bababyev, M. G. Volkov and V. T. Zabolotnyy,  
Moscow]

[Abstract] Buildup of volume defects of bombarding high-energy electrons, determining the radiation resistance of structural materials used in nuclear technology, is analyzed on the basis of an experiment and correlation of its results with the McKinley-Feshbach model. Wire specimens of technically pure tungsten, 50  $\mu\text{m}$  in diameter with a 5  $\mu\text{m}$  thick anticorrosive coating, were exposed to electron bombardment at the exit of Mikrotron-T accelerator outside its vacuum system. While being bombarded with a 21 MeV electron beam at a current density of 5  $\mu\text{A}/\text{cm}^2$  to a fluence of  $8.2 \cdot 10^{18} \text{ cm}^{-2}$ , the targets were cooled with water to a stable temperature near room temperature. After bombardment these wires were formed into cutting edges for autoion-microscope examination at a temperature of 78 K. The cross-section for formation of vacancy clusters and recoil atoms covering the energy range which corresponds to knockout of primary atoms into a displacement spike, 3.9 b according to calculations based on the experimental data, is fairly close to 3.2 b based on the McKinley-Feshbach model with a point nucleus. The authors thank A. L. Suvorov and L. I. Ivanov for assisting in the autoion-microscope examination. References 8: 5 Russian, 3 Western (2 in Russian).

2415/12223

CSO: 1842/82



UDC 621.315.592

DEEP PLASMOCHEMICAL ETCHING OF Si THROUGH DOUBLE-LAYER MASKS

Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 6, Nov-Dec 86 (manuscript received 26 Mar 86) pp 69-71

[Article by M. V. Varlamov, V. Yu. Kireyev and V. M. Frolov, Moscow]

[Abstract] Plasmochemical etching of Si single crystals, characterized by high speed under bombardment by low-energy ions, was studied experimentally for determining the feasibility of increasing the anisotropy index. The etching rate is known to be higher in a fluorinated medium than in a chlorinated one, but the resulting anisotropy to be weaker. Disks cut from KDB-12(100) and KEF-4.5(100) Si single crystals 76 mm in diameter were etched through masks in an apparatus consisting of a reactor with grounded shield, a 440 kHz ignitron, and a d.c. voltage source. A 0.2  $\mu\text{m}$  thick Al layer, a 0.2  $\mu\text{m}$  thick  $\text{Al}_2\text{O}_3$  layer, a 1.0  $\mu\text{m}$  thick photoresist FP-383 layer were used as masks. According to the results of examination under a NU-2E optical microscope with x1000 magnification and under a scanning electron microscope, the anisotropy after etching in a fluorinated medium increased from an index  $A=4$  when etching was done through an Al mask alone to an index  $A=10$  when etching was done through a double layer mask of 0.8  $\mu\text{m}$  thick FP-383 photoresist and 0.2  $\mu\text{m}$  thick Al. An  $\text{Al}_2\text{O}_3$  mask yielded an anisotropy index  $A=5$  and a FP-383 +  $\text{Al}_2\text{O}_3$  mask yielded an anisotropy index  $A=7$ . References 4: 2 Russian, 2 Western.

2415/12223

CSO: 1842/82

EFFECT OF REFRACTORY ELEMENTS ON RELAXATION RESISTANCE OF  
HIGH-TEMPERATURE ELINVAR ALLOYS

Moscow IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: CHERNAYA  
METALLURGIYA in Russian No 2, Feb 87 (manuscript received  
19 Feb 85) pp 63-67

[Article by O. A. Khomenko, S. B. Mikhaylov and  
A. V. Sazyakina, Ural Polytechnical Institute]

[Abstract] Stress relaxation in three series of Fe-Ni-Co elinvar alloys with 20% Co and up to 6.6% of any of the three refractory elements Nb, Mo and W, as well as dispersion hardening 2.6-3.0% Ti and 0.42-0.60 Al, was studied after either dual heat treatment or thermomechanical treatment. The experiment was performed with 0.35 mm thick and 4 mm wide ribbons of these alloys. Some specimens were heat treated by first quenching from 1050°C in water and then tempering at 700°C for 6 h. Other specimens were also quenched from 1050°C in water, then cold rolled to 20% or 50% reduction, and then tempered at 600-650°C for 6 h. Stress relaxation from the initial level of 589 MPa was monitored for 800 h. The results indicate that adding Nb effectively increases, while adding Mo or W does not increase, the relaxation resistance after plain dual heat treatment, while adding Mo or W increases the relaxation resistance after thermomechanical treatment more effectively than does adding Nb. In the latter case the relaxation resistance was found to be highest after rolling to 20% reduction, at temperatures not higher than 300°C to increase monotonically with increasing concentration of a refractory element, and at any temperature above 300°C to be maximizable by the corresponding optimum combination of refractory alloying element and heat treatment. References 3: all Russian.

2415/12223  
CSO: 1842/94

HIGH-PRESSURE FURNACE FOR SINTERING REFRACTORY COMPOUNDS

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 13 Mar 86) pp 9-11

[Article by P. S. Kisliy, A. A. Shamray and Ya. A. Kryl,  
Superhard Materials Institute, UkSSR Academy of Sciences]

[Abstract] The process of high-temperature gas-static powder compaction is examined, this process being particularly suitable for sintering refractory ceramic materials such as nitrides. The three major problems are attainment and maintenance of sufficiently high temperatures, nitrides requiring at least 1800°C, providing a sufficiently large gas-static working area, and avoiding significant temperature changes in that space during shrinkage of a compact, especially one of ultrafine-disperse material such as  $\text{Si}_3\text{N}_4$  powder. An electric furnace developed and built at the Superhard Materials Institute is capable of compacting powder under a pressure up to 10 MPa at temperatures up to 2000°C within a working area 400 mm high and 200 mm in diameter, with an available installed power of 142.2 kW. It consists of a heater, a high-pressure vessel as heating chamber, an open water-cooling system, a vacuum system for prevacuumization to a 5 Pa level, a gas feed system, and controls. It is provided with adequate thermal insulation, cooling jacket, fire resistant shield, O-ring seal, and quartz window for inspection. Either nitrogen or argon is used as working gas. References 10: 2 Russian, 8 Western.

2415/12223  
CSO: 1842/95

KINETICS OF  $TiAl_3$ -PHASE FORMATION IN Ti-Al SYSTEM

Kiev POROSHKOVAYA METALLURGIYA in Russian No 2, Feb 87  
(manuscript received 13 Feb 86) pp 26-31

[Article by V. N. Yeremenko, Ya. V. Natanzon and V. Ya. Petrishchev, Institute of Materials Science Problems, UkSSR Academy of Sciences]

[Abstract] Formation of the  $TiAl_3$  phase in a Ti-Al system and the kinetics of this process are analyzed, available data indicating that diffusional transfer is its basic mechanism. It has also been established that  $TiAl_3$  is the only intermetallic phase precipitating from Ti-Al vapor, absence of other phases such as  $Ti_3Al$ ,  $TiAl$  and  $TiAl_2$  after annealing being evidently a consequence of their very low growth rate rather than inhibited nucleation. The law of  $TiAl_3$  growth kinetics has been found to be almost linear  $x^{1.1+0.1} = kt$  for the initial approximately 40 h in Ti-Al vapor at a temperature of  $625^\circ C$ , exactly linear  $x=kt$  during the initial stage in  $Ti(5-25\%)Al^*-Al$  vapor, and parabolic  $x^2=kt$  throughout in  $TiAl-Al$  vapor. Interaction of Ti with solid Al and with liquid Al is further analyzed with the aid of thermodynamic and structural data. With the Arrhenius equation as reference, interaction rate constants are calculated as functions of time and of temperature in addition to the activation energy. The results indicate that transfer of Al, solid or liquid, to the reaction front and subsequent chemical interaction are not the limiting stages in buildup of a  $TiAl_3$  layer. References 13: 5 Russian, 8 Western.

2415/12223  
CSO: 1842/95



## ALLOYING BY LASER TREATMENT

Moscow METALLOVEDENIYE I TERMICHESKAYA OBRABOTKA METALLOV in  
Russian No 3, Mar 87 pp 14-20

[Article by L. S. Lyakhovich, S. A. Isakov, V. M. Kartoshkin  
and V. P. Pakhadnya, Belorussian Polytechnical Institute and  
Mogilev Technological Institute

[Abstract] A review of the state of the art in surface hardening and alloying of metals by laser treatment reveals two ways in which surface layers are produced, namely by implantation of borides, carbides, nitrides, or oxides, and by formation of hardening phases directly during the alloying process. Available data indicate that the hardened layer consists of two zones. The alloy zone, liquid during treatment, absorbs the added elements. The thermal influence zone remains solid during treatment but heats up. Formation of the alloy zone depends largely on the thickness of the alloying paste, on the speed at which the treated surface moves under the laser beam, and on the power density or the defocusing of the laser radiation. For a most reliable and correct performance evaluation, the last two factors are combined into a single composite parameter. A continuous-wave CO<sub>2</sub>-laser has been found to be most suitable for surface hardening and alloying. The structure of the alloy zone depends on the concentration of added elements, their concentration increasing as the speed of the moving surface is increased and as the laser power density is lowered so that the same amount dissolves in a smaller molten volume. The authors have confirmed these basic rules of alloy zone formation by experimenting with boron impregnation of steel, followed by structural examination and phase analysis in a DRON-3.0 X-ray diffractometer using CoK<sub>α1,2</sub>-radiation sources. They also experimented with increasing the concentration of alloying elements so as to produce new phases for an evaluation of their possible beneficial effects. More extensive use of laser treatment for surface hardening and alloying is still impeded by high cost and by scarcity of the necessary equipment as well as by the intricacy of this technology and the very high skill required for the operation. References 26: 19 Russian, 7 Western.

## WAYS TO INCREASE EROSION RESISTANCE OF POWDER STEEL

Moscow METALLOVEDENIYE I TERMICHESKAYA OBRABOTKA METALLOV in  
Russian No 3, Mar 87 pp 23-25

[Article by P. A. Kulu, Tallinn Polytechnical Institute]

[Abstract] An experimental study of St45 carbon steel produced by powder metallurgy was made for the purpose of evaluating its resistance to abrasive erosion in a gas stream and for finding ways to increase that resistance. Tests were performed in a TsUK-3M centrifugal accelerator with quartz sand of the 0.1-0.3 mm grain size fraction impinging on the steel surface at angles of 30-90° and at velocities up to 80 m/s. The dependence of the erosion resistance on the porosity of the powder steel was measured by testing specimens hot wrought to porosity levels ranging from 5% to 50%, with a specimen of cast St45 carbon steel normalized to a 200 Vickers hardness number serving as reference. The erosion resistance was found to decrease sharply with the porosity increasing from 5% to 10% and then again with the porosity increasing beyond 25-30%. For the purpose of increasing the erosion resistance, specimens were surface alloyed thermochemically by the diffusion process (carburizing, carburizing + case hardening, boron impregnation, chromium impregnation, chromium impregnation + case hardening, carbochromium impregnation, carbochromium impregnation + case hardening), coated by hardfacing (gas flame, plasma beam) and coated by spraying (plasma, sputtering). Thermochemical treatment, which results in formation of carbides, and sputtering of or hardfacing with composite powders ( $\text{Cr}_3\text{C}_2 + \text{Cr18Ni10}$ ), which results in buildup of coatings with the optimum combination of hardness and plasticity were found to be most effective. References 4:  
11 Russian.

2415/12223

CSO: 1842/96

UDC 620.193.1:621.793

EFFECT OF HEAT TREATMENT AND THERMOCHEMICAL TREATMENT ON  
PROPERTIES OF HARD POWDER ALLOYS

Moscow METALLOVEDENIYE I TERMICHESKAYA OBRABOTKA METALLOV in  
Russian No 3, Mar 87 pp 41-42

[Article by Yu. Yu. Pirso and Ya. P. Kyuvarsepp, Tallinn  
Polytechnical Institute]

[Abstract] Three hard powder alloys ( $WC_{15}$ ,  $Cr_3C_2+25\% Ni$ ,  $TiC+50\%Cr_{15}$  steel) were experimentally heat treated and thermochemically treated for an improvement of their erosion resistance and flexural strength. Heat treatment involved annealing at  $900^{\circ}C$  for 4 h in an  $Al_2O_3$  or  $SiO_2$  sand bed and in a hydrogen atmosphere. Thermochemical treatment at  $1000^{\circ}C$  for 4 h consisted of nitriding, boron impregnation, or phosphating with  $SiO_2+1\% (NH_4)_2HPO_4$  or  $Al_2O_3+50\%Fe_3P$ , also in a hydrogen atmosphere (except nitriding). Erosion by a water stream containing 5% quartz powder of the 0.1-0.3 mm grain size fraction and impinging at a velocity of 7.5 m/s was measured in a Stauffer centrifugal accelerator by weighing on an analytical balance. Phosphating was found to have produced the best results. References 6: 1 Russian, 1 East German, 4 Western.

2415/12223

CSO: 1842/96

UDC 669.295:536.421

DEPENDENCE OF PHASE COMPOSITION OF VT23 TITANIUM ALLOY ON  
HEATING TEMPERATURE AND COOLING RATE

Moscow METALLOVEDENIYE I TERMICHESKAYA OBRABOTKA METALLOV in  
Russian No 3, Mar 87 pp 60-63

[Article by A. A. Ilin, M. Yu. Kollerov, M. G. Ekimyan and  
V. V. Alekseyev, Moscow Aviation Technological Institute and  
Moscow Znaniya Truda Machine-Building Plant]

[Abstract] Phase composition of the VT23 titanium alloy (4.0-6.3% Al, 4.0-5.0% V, 1.5-2.5% Mo, 0.8-1.4% Cr, 0.4-0.8% Fe) was studied for the purpose of determining its dependence on the treatment temperature and on the cooling rate. Cubes of this alloy with 15 mm long sides cut from hot rolled stock were heated to temperatures of 720-950°C. They were then cooled at rates of 2-600°C/s by a jet of compressed air with a controllable water supply, at rates of 0.05-2°C/s in a container with sand, and at rates of 0.005-0.05°C in a programmed electric furnace. The cooling rate was measured and averaged over the 600-400°C range. Phase analysis was done in a DRON-3.0 X ray diffractometer with filtered CuK<sub>α</sub>-radiation. The results are presented in the form of a phase constitution diagram in the T(°C)-v(°C/s) plane. They indicate that both the equilibrium cooling rate and the critical cooling rate (minimum cooling rate for nondiffusional  $\beta$ -phase transformation) decrease as the heat treatment temperature is lowered, with an attendant narrowing of the range of cooling rates for  $\beta$ -phase decay by the intermediate (redistribution) mechanism. References 6: all Russian.

2415/12223  
CSO: 1842/96



UDC (621.791.753.5.052:621.039.5):620.17

MECHANICAL CHARACTERISTICS OF WELDED JOINTS IN COMPONENTS OF  
VVER-1000 MW WATER-MODERATED WATER-COOLED POWER REACTORS

Kiev AVTOMATICHESKAYA SVARKA in Russian No 1, Jan 87  
(manuscript received 16 Sep 85, in final version 21 Feb 86)  
pp 47-52

[Article by A. S. Zubchenko, doctor of technical sciences,  
S. I. Nosov, candidate of technical sciences, A. A. Popov,  
candidate of technical sciences, S. A. Shpak, engineer, and  
A. G. Mazepa, candidate of technical sciences, Central Scientific  
Research Institute of Machine Building Technology Scientific-  
Industrial Association]

[Abstract] An experimental study of welded joints in VVER-1000 MW and AST-500 MW power reactors was made, 15Cr2NiMoV-A steel (0.16% C, 2.05% Cr, 1.15% Ni, 0.54% Mo, 0.40% Mn, 0.29% V, 0.26% Si, 0.10% Cu, 0.014% P, 0.012% S) and the slightly better grade 15Cr2NiMoV-AA with less Cu, P, S though slightly more C being used as the principal structural materials. Welding is done with RT-45 electrodes using SV-12Cr2Ni2Mo-AA wire and FTs-16 flux. The purpose of the study was to determine the dependence of their mechanical characteristics and performance on their post-welding heat treatment. Specimens of both steels 190-230 mm thick with circular or butt seams produced by welding at a rate of 26-30 m/h with a current of 600-650 A under a voltage of 30-34 V were annealed, some at 620°C for 5 h only, others at 620°C for 18-25 h and then at 650°C for 9-20 h. After being subsequently soaked at the typical reactor operating temperature of 350°C for 3000-10,000 h, they were tested mechanically under static tension and under cyclic tension at a frequency of 20 Hz for cold shortness and fatigue resistance. The results indicate that final annealing at 650°C for up to 9 h ensures adequate mechanical characteristics of such welded joints. References 10; all Russian.

2415/12223  
CSO: 1842/79

UDC 621.791.4:539.378.3:(666.31.7+669.3)

DIFFUSION WELDING OF MULLITE-CORUNDUM CERAMICS THROUGH COPPER INTERLAYER

Kiev AVTOMATICHESKAYA SVARKA in Russian No 1, Jan 87  
(manuscript received 4 Mar 86) pp 72-73

[Article by R. A. Musin, candidate of technical sciences, Ya. V. Lyamin, engineer, M. Yu. Shabskiy, engineer, and G. F. Dobrynin, engineer, Perm]

[Abstract] Weldability of UF-46 mullite-corundum ceramics through a Cu interlayer was examined on the basis of a mathematical experiment. A physical experiment with diffusion welding of such a material in an A-306.04 automatic welding machine under vacuum has yielded  $1303 \pm 10$  K as the optimum temperature range. Three factors determining the mechanical strength of such joints were varied, namely contact pressure, welding time, and interlayer thickness. The resulting regression equation, tested for adequacy according to Fisher's criterion with 5% significance level, has yielded 15-25 MPa, 1-2 h, and 30-300  $\mu\text{m}$  respectively as the adequate ranges for this process. Microstructural examination of samples has, indeed, revealed no diffusion zones but rather an adjustment of the Cu lattice to the ceramic lattice. References 3: all Russian.

2415/12223  
CSO: 1842/79

UDC (621.791.75.052(204):669.15-194.2):(669.785+669.111)

DEPENDENCE OF  $H_2$ , C,  $N_2$ ,  $O_2$  DISTRIBUTION IN WELDED JOINT  
PRODUCED UNDER SEA WATER ON SALINITY OF LATTER

Kiev AVTOMATICHESKAYA SVARKA in Russian No 1, Jan 87  
(manuscript received 30 Dec 85) pp 75-76

[Article by O. D. Smiyan, candidate of technical sciences and  
V. Ya. Kononenko, engineer, Electric Welding Institute imeni  
Ye. O. Paton, UkSSR Academy of Sciences]

[Abstract] Rollers of 09Mn2Si steel (0.095% C, 1.65% Mn, 0.7% Si, 0.023% S, 0.015% P) were experimentally welded together under water, the purpose being to determine the dependence of  $H_2$ , C,  $N_2$ ,  $O_2$  distribution in the seam and in the thermal influence zone on the salt concentration in that water. They were faced 0.4 m below the surface of water in which the salt concentration was varied from 0 to 30%. Welding was done with PPS-AN1 powder-metal wire in an A-1742 laboratory machine at a rate of 7 m/h, with the current of 180-190 A at a voltage of 30-32 V. The joints were immediately cooled in liquid nitrogen for metallographical examination and chemical analysis. Topograms based on the data indicate that as the salinity of water increases, the overall  $H_2$ , C,  $N_2$  content decreases appreciably in both the thermal influence zone and in the seam while the  $O_2$  content also decreases in the thermal influence zone but increases somewhat in the seam. At the same time, however, the segregation of all four elements increases throughout. Since the cooling rate increases with increasing salt concentration, stresses in the metal and its hardness will also increase. Inasmuch as compressive stresses decrease with increasing  $H_2$  content, according to the Gorskiy effect, the stresses produced upon cooling must be compressive except very close to the fusion line. References 2: both Russian.

2415/12223  
CSO; 1842/79

UDC 621.791.72

**FORMATION OF FRONT WALL OF METAL MELTING CHANNEL DURING  
ELECTRON-BEAM WELDING**

Moscow FIZIKA I KHIMIYA OBRABOTKA MATERIALOV in Russian No 1,  
Jan-Feb 87 (manuscript received 9 Jun 86) pp 116-118

[Article by V. Ya. Belenskiy, Perm]

[Abstract] Formation of the front wall of the melting channel under an electron beam normally impinging on the metal surface during electron-beam welding is analyzed on the basis of a geometrical model where the front wall extends from the metal surface polygonally into the metal volume and moves with the electron beam parallel to the metal surface. Multiple reflections of the electron beam by successive straight wall segments as it penetrates into the metal and oscillatory shifting of the impact zone during the welding process are taken into account. The equation of heat balance is formulated for this geometry and a recurrence relation is established for the lengths of successive wall segments. A numerical solution of the problem on a programmable MK-56 microcalculator, assuming a conical electron beam with uniform radial power density distribution for welding steel parts, yields the beam radius in various given focusing configurations as well as the geometrical parameters of the front wall necessary for determination of the welding rate. References 4: 2 Russian, 2 Western (1 in Russian).

2415/12223  
CSO: 1842/93

UDC 621.791.4:539.378.3:621.9.02

**DIFFUSION WELDING OF CoNiTi16 TUNGSTENLESS HARD ALLOY TO  
BBCr15 BALL-BEARING STEEL**

Moscow SVAROCHNOYE PROIZVODSTVO in Russian No 2, Feb 87  
pp 18-19

[Article by G. A. Shchepetina, engineer, N. A. Mashkova, engineer, V. P. Antonov, candidate of technical sciences, and S. D. Lazarev, engineer, Moscow Aviation Technological Institute imeni K. E. Tsiolkovskiy]

[Abstract] An experimental study was performed for development of a technology for producing high-quality welded joints between CoNiTi16 tungstenless hard alloy and BB-15Cr ball-bearing steel parts. Cylindrical specimens of both materials having a 10 mm diameter and a 125  $\mu\text{m}$  surface roughness were welded together by the diffusion method under vacuum in an SDVU-70 machine with radiative heating at temperatures of 1273-1423 K with a contact pressure of 10-15 MPa and a 15-60 min long isothermal holding time. Welding was done directly and with an interlayer of 100  $\mu\text{m}$  thick Ni foil, 20  $\mu\text{m}$  thick fine-disperse powder compact, or 120  $\mu\text{m}$  thick combination of both. The joints were tested in an "Instron" 1185 machine for shear strength at a deformation rate of 1 mm/min. The results of these mechanical tests as well as X-ray micrography with a "Camebax" probe and fractography with an MBS-2 instrument indicate that the strongest joints are produced by welding with a 120  $\mu\text{m}$  thick combination interlayer of Ni foil and powder. References 3: all Russian.

2415/12223  
CSO: 1842/80



## REDUCING RESIDUAL STRESSES IN WELDED METAL-GLASS JOINTS

Moscow SVAROCHNOYE PROIZVODSTVO in Russian No 2, Feb 87  
pp 23-24

[Article by V. A. Bachin, candidate of technical sciences, V. N. Gasteva, candidate of technical sciences, G. B. Sukharev, engineer, and V. V. Shiryagin, engineer, Moscow Aviation Technological Institute imeni K. E. Tsiolkovskiy]

[Abstract] Specimens of KU5 quartz glass were experimentally welded together through an aluminum interlayer and the joints were then examined by the method of holographic interference with double exposure. The purpose was to determine the dependence of residual stresses on the interlayer thickness and to develop a heat treatment which would most effectively reduce them. Glass specimens  $15 \times 15 \text{ mm}^2$  in cross-section and 10 mm long were welded together through 0.1-0.8 mm thick aluminum interlayers in an SDVU-40 machine under vacuum at a temperature of 823 K, with a contact pressure of 8.0 MPa and a 30 min long isothermal holding time. The residual stresses were found to have increased from 9.1 MPa with a 0.1 mm thick interlayer to 29.4 MPa with a 0.8 mm thick one. Neither continuous cooling nor stepwise cooling with isothermal holding periods reduced residual stresses to below safe level, but cyclic annealing immediately after welding did. The effectiveness of this method was found to increase with increasing difference between upper temperature  $T_w$  equal to the welding temperature (823 K) and lower temperature  $T_c$ , a difference smaller than 50 K rendering the treatment ineffective, but a difference larger than 250 K with  $T_c$  below 573 K causing the glass to crack. The optimum lengths of holding time at both temperatures were found to be 20-30 min, and the interlayer thickness could be increased to  $h = h_0(T_w/T_c)$  ( $h_0$  - thickness for welding without subsequent annealing) for better joint matching. References 3: all Russian.

2415/12223  
CSO: 1842/80

THE SCIENTIFIC-TECHNICAL REVOLUTION AND MINERALS

Moscow PRIRODA in Russian No 2, Feb 87 pp 89-98

[Article by L. V. Tauson: "NTR and Minerals"]

[Text] Minerals have always been one of the most important foundations of the economy. Virtually every civilization has depended on the availability and ability to find and recover them. However, the 20th century holds a special place in history. It has been marked by great social, scientific, and technical revolutions which drastically have altered people's way of life. At this time in the history of mankind the use of minerals has increased at an entirely astounding rate, and the types of minerals use considerably expanded.

Technological Stage of NTR [the Scientific-Technical Revolution]

Mineral consumption rates particularly rose at the technological stage of the scientific-technical revolution, the beginning of which is taken to be 1960. This stage is characterized by an abrupt intensification of the process by which scientific knowledge is materialized, which is expressed in the creation of new technologies and machines and their use in industry and the appearance and widespread use of computers.

The rate of growth of mineral recovery at the technological stage of the scientific-technical revolution is especially apparent in the example of copper. Mankind has used copper for almost 10,000 years (the alloy produced with copper did not give its name to the long period in the history of material culture — the Bronze Age — in vain). It has been calculated that, over the entire history of mankind, 270 million tons of copper have been mined from the Earth's interior. However, before the 20th century, only 35 million tons had been extracted, while in this century the level of annual recovery rose from 0.5 million tons in the first decade to 8 million tons in the next to last. As a result, from 1960 to 1985 alone 155 million tons were mined, i.e. more than half the amount mined in all previous history. By the year 2000 the level of copper mining will apparently reach 10-12 million tons a year. Because of such a rapid increasing in recovery, poorer and poorer ores are being put to use. While it was considered profitable to extract ore containing 4 percent copper at the beginning of

the century, now ore with only about 0.5 percent copper is taken in open pit mines in major deposits. This decline in ore quality is a trend typical of many metals.

The growth in recovery of minerals which mankind has begun using only in the 20th century is accelerating. These include petroleum, natural gas, aluminum, uranium, and many rare metals. Among metals, production and consumption of aluminum grew particularly quickly. Even in 1950 its annual production was about 1 million tons; by 1960 it had increased to 4 million; and by 1975 it surpassed 11 million tons. Since then annual aluminum output has varied between 12 and 14 tons. Just as astounding were the rates of recovery of mineral fuels, especially petroleum and gas. This is clearly seen in our country. In 1945 we recovered only 3 billion cubic meters of natural gas, 643 billion 40 years later. This drastic increase in recovery (more than 200 times) became possible primarily because of the discovery of giant gas fields such as Urengoy and Yamburg in northern Tyumen Oblast. Natural gas is the best example of another trend in recovery of minerals in the technological stage of the scientific-technical revolution, typical for petroleum and many metals: large deposits are their main producers. The primary sources of petroleum are giant fields whose reserves are estimated at billions of tons. For example, the reserves of the world's largest petroleum field, Gkhavar in Saudi Arabia, are calculated at 11 billion tons. There are almost 15 such fields throughout the Near East, so that more than half the world's petroleum reserves are concentrated there.

The colossal growth in consumption of minerals, the tendency for working deeper mines to be exhausted, the development of poorer and poorer ores (which complicates ore mining and increases its net cost) have led to a sharp increase in the costs of almost all types of minerals. In the years of the energy crisis, 1973-1974, petroleum prices rose by a factor of almost 15; those of natural gas, by a factor of more than 10. At the same time, gold prices rose tenfold; tin, molybdenum, and chrome, sevenfold. However, the "champion" among metals has turned out to be tungsten, whose cost per ton rose from \$400 in 1955 to \$20,000 in 1980, i.e. by a factor of 50. The increase in raw materials prices predetermines the possibility of economically profitable use of poorer ores and the return to previously abandoned deposits. For example, gold mining in the United States has more than doubled in recent years, reaching 75 tons in 1985 — to a great extent because of these sources.

There are two other key factors affecting the economics of minerals: unequal consumption and unequal location of mineral deposits. In the United States, where about 5 percent of the Earth's population lives, aluminum and fuel consumptions per person, for example, are 70 and 60 times higher than in developing countries, where 70 percent of our planet's inhabitants live. Along with unequal consumption, the unequal distribution of major mineral fields is apparent. Several countries, particularly Japan, FRG, and Italy, are distinguished by a scarcity of mineral resources. Japan, for example, imports its entire petroleum consumption, a significant portion of its coal, 90 percent of its iron ore, etc. The unequal distribution of deposits has a



considerable effect on the world balance of reserves of many types of minerals.

#### Availability of Mineral Supply

Considering the problem of supplying mankind with minerals in the technological stage of the scientific-technical revolution, one must keep in mind that this stage is characterized by the birth of new technologies for prospecting, exploration, and exploitation of mineral deposits and creation of new technologies in power engineering, machine building, and other sectors of the national economy on the basis of new structural materials has led to a significant growth in the need for certain types of minerals for which there has never before been a demand. Moreover, in analyzing mineral problems, one never before been a demand. Moreover, in analyzing mineral problems, one must consider that the tremendous scales of consumption of traditional types of minerals will continue. One naturally asks to what extent mankind has been supplied with various types of minerals and whether it is threatened with their exhaustion.

The only mineral which could be used up in the next centuries is petroleum. The answer for other minerals is much more optimistic.

Even V. I. Vernadskiy showed that a dispersed form of matter predominates on the Earth. The current ratio of concentrated and disperse forms can realistically be estimated. Raw data for estimating are the content of an element in rock in the continental core, its quantity in rocks in the first kilometer of the continental core, and the total amount of proven and recovered reserves. The table provides this calculation for three metals.

Ratio of concentrated and dispersed forms of certain metals

| Metal   | Amount of metal                                                      |                                               |                                        |                                          |
|---------|----------------------------------------------------------------------|-----------------------------------------------|----------------------------------------|------------------------------------------|
|         | Average content in the first in rocks in the continental core, wt. % | in the first kilometer of continental core, t | Total proven and recovered reserves, t | Ratio of concentrated to dispersed forms |
| Iron    | 4.2                                                                  | $1.7 \cdot 10^{16}$                           | $8 \cdot 10^{11}$                      | 1/20,000                                 |
| Copper  | 0.01                                                                 | $4 \cdot 10^{13}$                             | $8 \cdot 10^8$                         | 1/50,000                                 |
| Niobium | 0.002                                                                | $8 \cdot 10^{12}$                             | $8 \cdot 10^6$                         | 1/100,000                                |

Only 1/20,000 of iron is in a concentrated state; for niobium, this form accounts for only one millionth of the dispersed substance. However, geologists are still not actively prospecting for niobium deposits. One might assume that even in the next decades its proven reserves will grow by an order or magnitude. On the other hand, prospecting geologists believe that the first kilometer of the continental core must contain about 7-8 times more ore deposits than already found. If proven copper reserves are

now estimated at 500 million tons, predictions show 3.5-4 billion tons. With an annual recovery of even 10 million tons, these reserves will last at least 4 centuries. But even in this case only 1/10,000 of the substance is in concentrated form.

Analysis of the level of exploration for minerals on Earth allows us to state that mankind is not threatened by any mineral famine. Given the ever increasing consumption of raw materials, we are only obliged to learn to find, recover, and process them more efficiently.

#### Aluminum — the Metal of the 20th Century

In the next decades we must pay special attention to minerals which will be in greatest demand at the technological stage of the scientific-technical revolution. This pertains primarily to aluminum and certain rare metals.

Aluminum is being increasingly used in the national economy, and its role would grow even more rapidly if it were not for energy, ecological, transportation, and economic problems related to its production. Aluminum is now 2.5 times more expensive than lead (\$1,140 vs. \$430 per ton) and close to copper. In the last 10 years, the annual world output of aluminum has varied around 12 million tons. The largest consumer is the United States, where 20 kg of aluminum are consumed annually per capita. There is no doubt that both developed countries (Japan, FRG) and those with basic reserves of raw aluminum (Australia, Guinea, etc.) will approach a high level of production and consumption in the 20th century. The major factors delaying the development of the aluminum industry will be the limited nature of energy capacities and the considerably rising cost of long-distance transport of raw material (bauxites). However, it is noteworthy that bauxite producing countries display a tendency to expand production of aluminum itself. At the same time, output of aluminum in highly developed countries, where there is an energy shortage and imports are required (Japan), is declining.

To ensure the growth of aluminum output in this country, we must clearly follow two mutually complementary paths. In addition to rebuilding, existing enterprises must make extensive use of lithium, which permits a 4-7 percent reduction in energy consumption, a 10 percent increase in strength of current, and a 20-50 percent decrease in fluorine release. Abroad lithium is used rather actively in the aluminum industry, and the technology for its application is well known. Meanwhile, it is quite desirable to develop new aluminum production processes which are less energy intensive and do not require bauxite as raw material. We already have many years of experience using nepheline syenites to obtain alumina. In addition, certain countries (Japan, USA) have devised new processes for obtaining aluminum (pyrometallurgical and hydrometallurgical), which are much less energy-intensive and allow other sources of this metal to be used. In the United States particularly, a hydrometallurgical technology has been developed in which aluminum is obtained from the ash from coal combustion. Our country has two basins whose brown coal ash contains 30-35 percent alumina:



**Ekibastuz in Kazakhstan and Azeyskiy in Eastern Siberia. Construction of aluminum plants based on TeTs fueled by this coal is quite realistic.**

**Finally, alkaline aluminosilicate rock — synnyrites, which are a complex raw material for producing silica and potassium — are a very promising source of aluminum.<sup>1</sup> There are now two huge massifs of this rock in the BAM [Baykal-Amur Line] area in Siberia: Synnyrsk and Sakunsk. It is quite important that the latter is in close proximity to the rail line in the Charek mining rayon and that its development does not require large expenditures.**

#### **Rare Metals in 21st Century Technology and Economy**

**The largest problem in the technological stage of the scientific-technical revolution is whether mankind can make extensive use of rare metals. The solution to this problem promises a revolutionary transformation in the technology and economy of the 21st century. Numerous studies and technological analyses performed mostly in the last 20 years have demonstrated the exceptional effectiveness of using rare metals in almost all sectors of the national economy. The fundamental importance of rare elements to ferrous and nonferrous metallurgy and commercial production of new composite materials, primarily ceramics, is now entirely obvious. Rare metals make it possible to create stronger alloys and alloyed steels, which possess good corrosion resistance, perform more efficiently at low and super-high temperatures, and bring about a substantial decrease in metal consumption in machinery production. Naturally, different alloys and composite materials obtained with rare elements greatly expand the opportunities for creating new generations of machines distinguished by increased strength-to-weight ratio and greater durability in extreme conditions.**

**Just as important in the future will be the use of rare metals in power engineering, especially thermonuclear. Specialists believe that consumption of lithium and niobium will increase at least tenfold and the use of beryllium, zirconium, vanadium, rare earths, etc. will rise considerably in the era of commercial thermonuclear power. Obviously, under these conditions a country's energy might will depend not only on the creative potential of its physicists and power engineers, but also on its output of rare metals.**

**One could name dozens of branches of industry where the use of rare elements even now promises a major economic effect. From this standpoint, meeting the needs for rare elements must be considered as one of the key factors in scientific-technical progress, especially in machine building, instrument building, and metallurgy. Regarding the raw material aspects of the technological stage of the scientific-technical revolution, let us present two very illustrative examples of the use of rare elements — lithium and niobium.**

**We have already noted the merit of using lithium in the aluminum industry. The efficiency here depends on the fact that lithium-containing electrolytes**

in electrolyzers possess a lower melting point and higher electrical conductivity. As a result, the electrolysis process is accelerated, electrolyzer productivity is boosted, electricity consumption drops, and much less fluorine is released (the last is particularly important for improving working conditions in electrolysis shops and for protecting the environment from the lethal effects of fluorine). The production of light and ultralight alloys, in which lithium is the main alloying component, promises at least equal savings. Its use will make it possible to produce structural materials with a specific gravity half that of aluminum with at least equal strength and superior ductility. We hardly need to prove the importance of these lithium-aluminum alloys for aircraft construction and space technology.

Lithium greases have been used for many years in different fields of technology. They are distinguished by high viscosity, longevity, insolubility in water, and stability over a wide range of temperatures. In the near future, lithium will be extensively used in chemical current sources, especially in lithium storage batteries which can become the most efficient sources of electricity for mobile means for different purposes. Consumption of lithium will repeatedly increase in the transition to the thermonuclear power engineering of the future because it is becoming the primary "raw material" for producing tritium, one of the major components of thermonuclear fuel and also a liquid heat transfer agent in thermonuclear reactors. The list of lithium's applications and scales of use could continue, but what has been said so far predetermines the need for a significant increase in output of this metal.

The world now produces 7,000 tons of lithium annually. The United States consumes 5,500 tons of this. According to specialists' calculations, world consumption of lithium by 2000 will rise to 80,000 tons, i.e., by more than 10 times, and may reach 120,000-140,000 tons by 2020. World lithium reserves are now estimated at 2.5 million tons; more than half of these are in the saltwater lakes of the Atacama Desert (Chile), while one-fifth is concentrated in the USA. We must add that American monopolies own 55 percent of the stock in lithium plants now being built in Chile--the United States considers lithium one of the most important strategic metals.

Niobium is another important rare metal which will be extensively used in the most diverse sectors of the natural economy. Ninety percent of all niobium is still consumed in metallurgy, and 60 percent of this is used in production of large-diameter pipe for petroleum and gas lines laid in regions with extreme climatic conditions. Niobium's specific applications result from the fact the steels alloyed with niobium are distinguished by much higher strength and lower cold shortness, which permits a significant decrease in pipe weight. In recent years Japan has become the largest producer of niobium steel pipe. Low-alloyed high-strength steel with niobium additives has turned out to be quite beneficial in production of heavy structures, building elements, and bridges, transportation and mining equipment and have made it possible to reduce their weight and prolong their service life. It is no accident that 33 percent of the niobium consumed in

the United States is used to manufacture metalworks, 32 percent for production of transportation equipment. Finally, niobium, along with tungsten, molybdenum, and tantalum now constitute the four rare metals from which heat-resistant alloys for aerospace equipment are made.

The use of niobium in an important field such as the production of superconductor materials will rise immeasurably in the near future. Transmission of electricity in superconductor cables is now becoming technically feasible. Cables made of Nb<sub>3</sub>Sn can carry current 10-100 times more powerful than that carried on modern power transmission lines, and losses are only 0.5 percent as opposed to the usual 3-10 percent.

In the near future, the unique superconducting properties of niobium and its compounds and alloys will be used more and more extensively in MGD [magnetohydrodynamic] generators and thermonuclear power engineering. It is not surprising that these properties of niobium have made it a key strategic metal. The cost of a ton of niobium on the world market is \$27,000, while world output is approaching 25,000 tons per year. According to current calculations, its consumption by the year 2000 will reach 100,000-150,000 tons and by the year 2020, given the development of commercial thermonuclear energy, demand may rise to an unbelievable number--600,000-800,000 tons per year.

As already mentioned, about 90 percent of the world's niobium reserves are concentrated in Brazil, primarily in the carbonatite deposits of Arash and Tapir. In these unique fields, estimated at about 7 million tons, the niobium pentoxide content varies from 3.5 to 4.5 percent, and the primary ore mineral is pyrochlore, considered the best raw material for producing ferroniobium. (For comparison: Canada's richest niobium carbonatite ores contain only 0.5 percent niobium pentoxide; Nigerian granites, no more than 0.25 percent). However, despite logic and justice, exploitation of the national riches of Brazil is to a great extent in the hands of U.S. monopolies.

Mankind's demand for rare metals is hardly limited to lithium and niobium. In the future they will be joined by certain rare earth elements -- beryllium, tantalum, vanadium, cadmium, and many others. Recognizing the importance of rare metals for 21st century technology, we must intensify efforts to find and evaluate their deposits and expand technological developments to extract rare metals from different types of raw minerals.

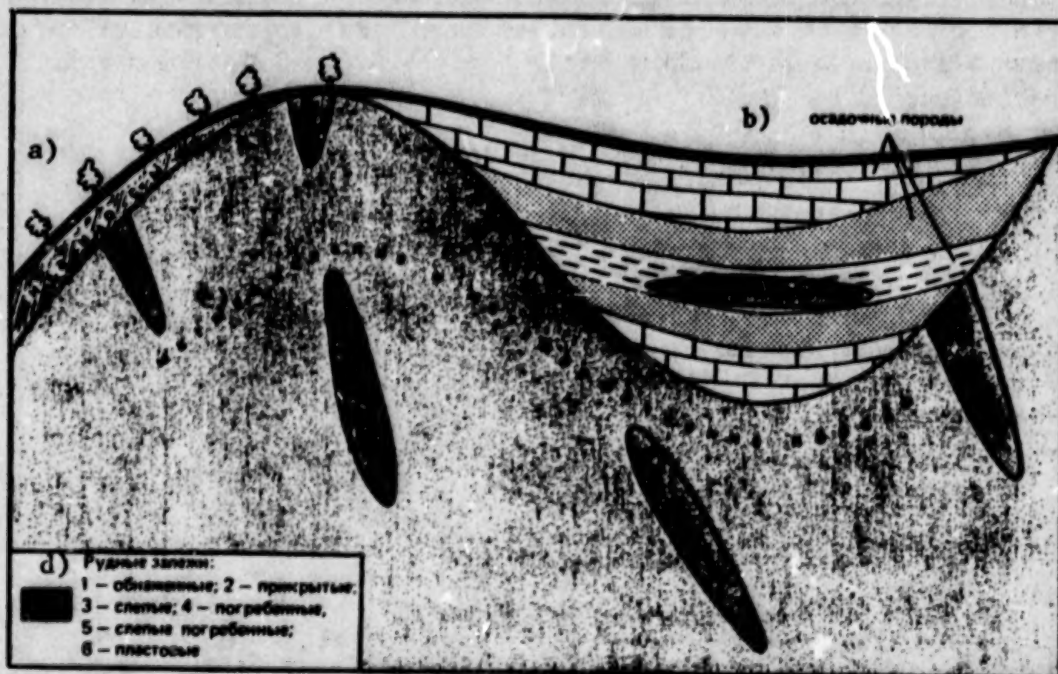
Naturally, the accent on the growing importance of rare metals does not preclude intense exploration for and recovery of other kinds of minerals. The 21st century is already assured of many minerals. However, given the current level of recovery, the proven reserves of some are not enough to last long. The situation with tungsten and tin is the most worrisome; to a lesser extent that of zinc, lead, copper, nickel, and molybdenum. Moreover, we must keep in mind not only the magnitude of proven reserves, but also the predicted resources -- and these are usually several times larger. Finally, the well known conditionality of the estimates of raw material supply is determined by the fact that the level of consumption assumed should not be



considered constant. It will rise in the 21st century because of the inevitable increase in consumption of minerals in developing countries.

### Strategy for Exploration for and Development of Minerals

The strategy for prospecting and exploring for mineral deposits must be substantially revised. The familiar problems of recovering solid minerals arise because of the imminent depletion of the stock of so-called easy to discover deposits exposed on the Earth's surface in economically developed regions. Admittedly, these deposits may still be found in little developed regions, where preparation for seam development requires major capital investment. The number of such undiscovered deposits in developing countries is particularly great. However, the number of seams which are not exposed on the surface -- and are hard to discover -- is immeasurably greater. Several basic types are distinguished, depending on the position of these ore bodies within a rock mass: exposed, covered, blind, buried, blind buried, and seam.



Classification of ore deposits as a function of their position in the rock mass.

Key:

- |                                |                  |
|--------------------------------|------------------|
| a) Detritus                    | 2 - Covered      |
| b) Sedimentary rock;           | 3 - Blind        |
| c) Magma and metamorphic rocks | 4 - Buried       |
| d) Ore deposits                | 5 - Blind buried |
| 1 - Exposed                    | 6 - Seam         |

Exposed deposits are considered easy to discover because they are found by surveying the Earth's surface. To find deposits of all other types, one

must prove a site in a working where, at the predicted depth, the ore body should be exposed. This can be done by finding various, indirect signs of the presence of deposits on the Earth's surface or in its depths. These signs may be detected by geological, geochemical, and geophysical methods. Therefore, creation of a new technology for exploration which incorporates not only geological but also geochemical and geophysical information on the structure of the areas studied must become a fundamentally new aspect of the prospecting strategy in the near future.

It is now clear that in many cases, individual deposits must be considered only as a component part of a whole, sometimes quite large, ore-bearing system. So-called ore-magma systems are especially important; mineral deposits in them are the products of metasomatic and hydrothermal processes in the Earth's core during the degassing and cooling of the magma flows which crystallized at a depth of 4-5 km (hypabyssal intrusions). The geochemical types of magma masses determined their ore-bearing potential and the set of deposits which can be formed in genetic relation with them. In many cases these ore-magma systems take the form of circular volcanic-plutonic structures within which dozens of deposits and ore manifestations are found. As has now been established, these structures are quite widely developed in intercontinental moving zones and have formed because of the intrusions of so-called latite magmas, which are distinguished by maximum ore-bearing potential for a large number of metals. For example, in the Eastern Zabaykal, at least 20 of these structures have now been counted. Naturally, in exploration one must take

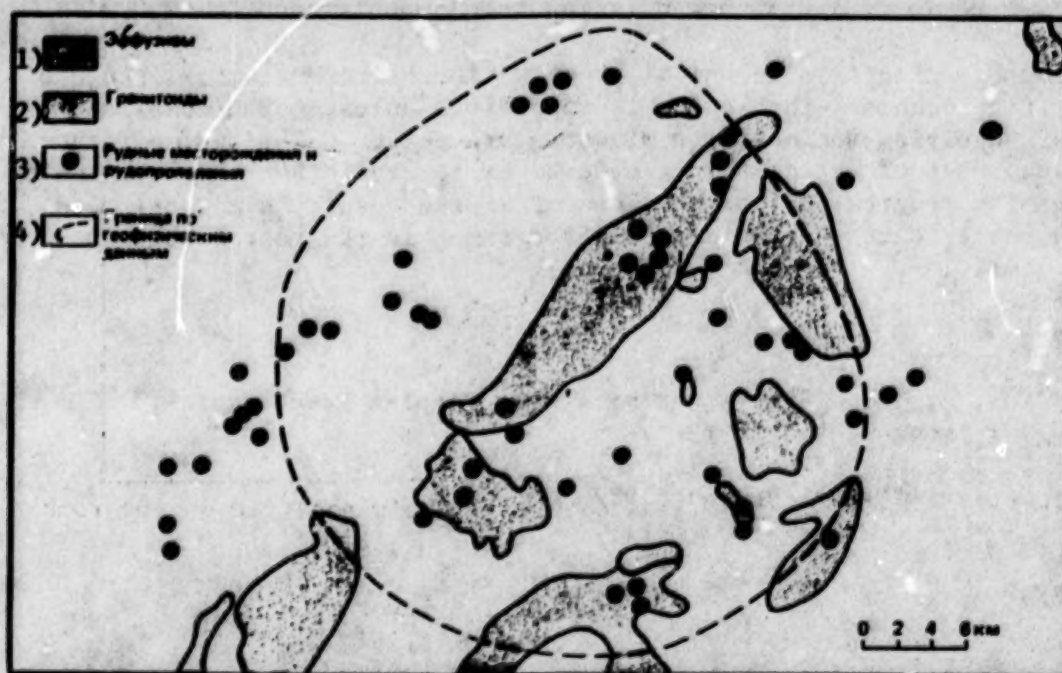


Diagram of a circular ore-magma system known to contain beds and shows of lead, zinc, tungsten, copper, golds, feldspar, etc. ores.

Key: 1) Effusions 3) Ore deposits and ore manifestations  
2) Granitoids 4) Boundary based on geophysical data



into account precisely the group arrangement of mineral deposits, and they must be developed comprehensively.

Comprehensive development should also be carried out in regions in which ore systems of various genetic types and deposits of different scales and composition are known. This most often pertains to newly developed ore regions and requires not only that recovery and primary processing enterprises be built, but also that the entire infrastructure which ensures normal social and domestic living conditions, transportation, the required energy resources, etc. be created.

All this dictates the need to revise the strategies for developing deposits as well. While development of deposits of noncombustible minerals by different departments may have been previously permitted, now, given the necessity of the comprehensive approach, they must be developed by an organization united administratively, financially, and managerially. It appears that under these conditions it is quite worthwhile to consider the question of combining all efforts to find, explore for, and exploit deposits of noncombustible minerals under a single Ministry of Geology and the Mining Industry.

To assure the country of a supply of all the required minerals, special attention must be given to the technical level of material base of the geological exploration and mining industry. This pertains both to mining equipment and to instruments for analyzing the composition of a mineral.

Acceleration of scientific-technical progress in the technological stage of the scientific-technical revolution is impossible unless quite complicated problems of supplying society with minerals are solved. Their significance in the development of our country's economy is so great that the creation of a comprehensive program for the development of the country's mineral base, similar in scale to the Energy and Food Programs, in the near future is extremely timely.

#### References

1. Cf. Zhidkov, A. Ya., "Synnyrites — A New, Complex Raw Material," PRIRODA, No. 5, 1986, pp. 96-101.

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**DATE FILMED**

8 Feb. 1988